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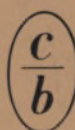
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LITHOLOGY AND MINERAL RESOURCES

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LITHOLOGY AND MINERAL RESOURCES

A translation of *Litologiya i Poleznye Iskopaemye*

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RARE-EARTH ELEMENTS AND LITHOFACIES ZONATION OF OCEANIC SEDIMENTS
(TRANS-PACIFIC PROFILE).

I. ZONAL DISTRIBUTION OF RARE-EARTH ELEMENTS IN SEDIMENTS

T. F. Boiko, N. A. Lisitsyna, and G. Yu. Butuzova

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The effect of continental and island sources of sediment supply on the distribution of rare-earth elements in bottom muds along a Trans-Pacific profile (Japan-Mexico), and the trends in content and composition of lanthanides toward pelagic areas, were examined. It is shown that rare-earth elements have a zonal distribution reflected in the lithofacies zonation of oceanic sediments.

In recently published articles on problems on the geochemistry of lanthanides and yttrium in the oceans, Fleet [13] and Humphries [14] correctly point out the contradictions in much of the available data on the distribution of these elements in various oceanic environments and the necessity for further studies in order to develop an accurate picture. The literature is particularly concerned with the source of rare-earth elements (REE) and yttrium in seawater and marine sediments; the role of biogenic, hydrogenic, and lithogenic aspects of their extraction from seawater and introduction into bottom muds; trends in fractionation of lanthanides in the ocean; zonal distribution of REE and Y in sediments; the possibility of lanthanide indicators for origin of oceanic oozes; the role of halmyrolysis in the REE composition of seawater, and the effects of halmyrolysis products on the composition of lanthanides in bottom sediments, etc. Reference lists of the basic literature on these themes are presented in [13, 14].

The authors of the present article have considered REE and Y in a lithologic, mineralogic, and geochemical study of sediments on a Trans-Pacific profile from the coast of Japan to the shores of Mexico (46th voyage of the research vessel Vityaz' and the ninth voyage of the research vessel Dmitri Mendeleev). Part of the results obtained have been published in a general form in [2]. A more detailed examination of the available information presented in that paper is dictated by the many problems concerning the distribution of REE and Y in the ocean.

The profile and the locations of observation stations along it are shown in Fig. 1. The coordinates of the stations and detailed lithologic, mineralogic, and geochemical descriptions of the bottom muds are presented in [4, 6].

From the continental coast to the deep marine basins, 12,000 km in length, the profile studied transects virtually every major tectonic structure of the northern Pacific Ocean. These are expressed in bottom topography, which makes it possible to examine the various sediments associated with particular tectonic and morphological features of the sea floor. As a result of detailed studies of their composition, several lithofacies of bottom muds typical of oceanic sedimentation [6] were recognized. Nearshore coarse-grained volcanic-terrigenous and biogenic-terrigenous sediments of the shelf and continental slope (zone I) grade into hemipelagic, clayey, slightly siliceous, slightly limy oozes of the deepwater trenches and margins of the ocean floor (zone II), and more distant, transitional pelagic clays of the periphery of the deep ocean basins (zone III), followed by pelagic red clays with volcanic ash (zone IVA) and with zeolites (zone IVB) of the main ocean basin. In the central part of the ocean, this succession is complicated by superposition of gravel-sand-clay and carbonate deposits against the general background of pelagic clay in the region of the mid-Pacific ridge (zone V) and of biogenic-terrigenous sediments containing some volcanoclastic material in the area of the Hawaiian Islands (zone VI). Zone VI is a natural boundary, separating the western part of the profile from the eastern.

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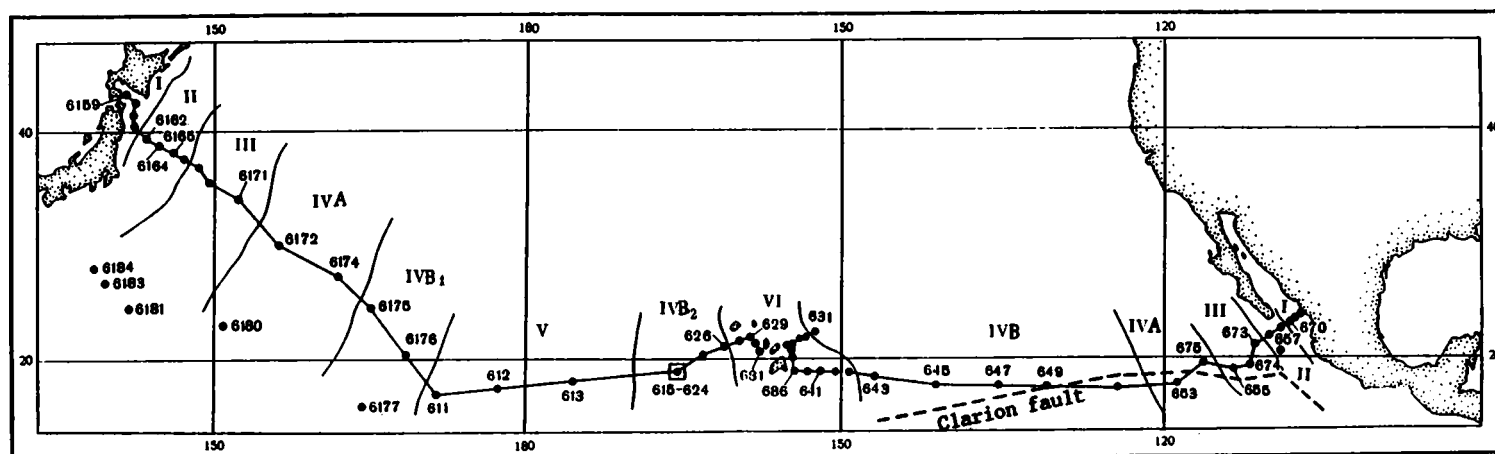


Fig. 1. Trans-Pacific profile. Dots indicate stations: I-VI are lithofacies zones.

TABLE 1. REE Content in Bottom Sediments of a Trans-Pacific Profile, g/ton

Zone	Station no.	La	Ce	Sm	Eu	Yb	Lu	Y	
I	6158	15,5	27,1	2,9	0,73	1,8	0,38	—	
	6159	12,0	21,4	2,7	0,63	1,4	0,36	25	
	6160	15,7	29,1	2,9	0,84	1,78	0,35	30	
	6161	15,3	25,0	2,5	0,54	1,44	0,38	30	
II	6162	—	—	—	—	—	—	32	
	6163	18	34	3,1	0,84	1,9	0,4	25	
	6164	17,5	35	3,7	0,90	2,3	0,4	23	
	6165	17	31	3,5	0,89	2,3	0,42	24	
III	6184	17	35	4,1	0,86	1,9	0,35	—	
	6171	22	48	4,5	1,20	3,0	0,44	32	
	6183	27	55	4,6	1,35	2,6	0,50	—	
	6181	—	—	—	—	—	—	24	
IVA	6172	29	61	4,5	1,2	3,0	0,44	50	
	6180	42	92	8,25	2,16	4,05	0,77	—	
IVB ₁	6175	40	70	6,5	1,7	1,9	0,35	40	
	6176	87	172	20,6	5,8	11,0	1,70	160	
	6177	—	—	—	—	—	—	100	
V	611	54 (82)	93 (142)	12,6 (19,2)	4,1 (6,3)	6,5 (9,9)	0,97 (1,48)	96 (147)	
	612	147	308	37	11	13,6	2,1	320	
	613	39 (84)	53 (115)	9,5 (20,6)	2,8 (6)	4,6 (10)	0,7 (1,52)	72 (156)	
IVB ₂	615	47	93	12	3,1	5,1	0,75	64	
	616	52	79	14	3,3	5,3	0,85	70	
	617	46	89	12	3,2	5,3	0,88	64	
	619	41	78	10	3,0	4,3	0,60	50	
	620	51	90	15	3,2	5,8	1,00	80	
	621	41	77	10	3,0	4,5	0,55	65	
	623	44	87	11	3,0	4,8	0,65	80	
	626	42	89	12	3,0	4,9	0,70	88	
VI	West	627	18	43	5,7	1,9	2,2	0,35	50
		628	19 (42)	30 (66)	4,7 (10,3)	1,6 (3,5)	2 (4,4)	0,35 (0,8)	30 (67)
		629	14 (39)	24 (67)	3,4 (9,5)	0,9 (2,5)	2,2 (6,1)	0,26 (0,73)	16 (45)
		681	24	44	7,9	2,5	2,5	0,8	40
	East	632	29	57	8	2,9	3,3	0,52	46
		633	17 (36)	36 (75)	5,6 (11,7)	1,5 (3,1)	1,6 (3,3)	0,26 (0,54)	16 (33)
		634	32	61	9,4	2,6	3,2	0,48	46
		635	15 (31,5)	31 (65)	3,6 (7,5)	0,8 (1,7)	1,7 (3,6)	0,26 (0,54)	24 (50)
		636	24	48	5,7	2,9	3,3	0,35 (0,52)	24
		637	15 (25)	36 (61)	4,5 (7,6)	1,7 (2,9)	1,1 (1,9)	0,26 (0,44)	34 (56)
		638	16 (24)	31 (51)	5,3 (8,0)	1,7 (2,5)	2,1 (3,1)	0,35 (0,52)	16 (24)
		686	24	40	4,7	2,7	3,2	0,6	24
		641	19	48	5,5	1,9	2,7	0,35	16
		678	23	43	6,4	2,3	3,2	0,62	40
		677	30	49	7,9	2,0	3,2	0,52	46
IVB	Eastern half of profile	651	—	—	—	—	—	—	90
		631	42	81	9	3,0	5,0	0,76	48
		643	46	97	12	3,3	5,0	0,70	72
		645	51	99	11,6	2,8	5,3	0,90	104
		647	43	86	9	3,1	5,0	0,80	64
		649	44	82	9,4	2,8	5,4	0,84	64
		653	70	121	13,6	4,5	7,5	1,3	96
		675	59	97	16	4,3	6,7	1,1	112
III		655	45	89	10,4	3,0	5,1	0,97	88
		674	43	83	9,6	3,0	4,8	0,94	86
		673	41	65	9,1	2,4	4,6	0,88	56
II		672	22	46	4,5	1,2	1,6	0,36	32
		671	22	35	4,5	1,1	2,6	0,44	28
		657	26	45	4,8	1,3	2,8	0,4	48
I		670	22	37	4,7	0,95	2,6	0,46	29
		669	24	39	4,7	0,9	2,4	0,44	50
		668	27,8	48	4,9	1,1	3,1	0,54	34

Note. Numbers in brackets are recalculated as carbonate-free.

TABLE 2. Average Content of Elements in the Surface Layer of Sediments along a Pacific Profile by Lithofacies Zone

Element	Western part of profile						
	I	II	III	IVA	IVB ₁	V	IVB ₂
La	14,6	17,5	22	35,5	63,5	81 (104)	45
Ce	25,6	33	46	76,5	121	151,3 (188)	85,2
Sm	2,75	3,4	4,4	6,4	13,5	19,7 (25,6)	12
Eu	0,68	0,87	1,14	1,68	3,75	6,0 (7,8)	3,1
Yb	1,6	2,1	2,5	3,52	6,4	8,2 (11,2)	5,0
Lu	0,37	0,4	0,43	0,60	1,0	1,26 (1,7)	0,75
ΣTR	45,6	57,3	76,5	124,2	209,1	266,4 (338)	151,0
Y	28,3	26	28	50	100	163 (208)	70
P	0,06	0,05	0,06	0,06	0,22	0,24 (0,37)	0,14
Mn *	—	0,22	0,30	0,38	0,36	0,38 (0,45)	0,36
Fe *	—	0,39	0,48	0,47	0,46	0,37 (0,45)	0,54

Element	Hawaiian islands	Eastern part of profile				
	VI	IVB	IVA	III	II	I
La	21 (29)	45	64,5	43	23,3	24,6
Ce	39 (55)	89	109	79	42	40,4
Sm	5,7 (7,9)	10,2	14,8	9,7	4,6	4,76
Eu	1,9 (2,5)	3	4,4	2,8	1,2	0,98
Yb	2,4 (3,4)	5,1	7,1	4,8	2,3	2,7
Lu	0,44 (0,60)	0,80	1,2	0,93	0,40	0,48
ΣTR	70,4 (98,5)	153,1	201,0	140,2	73,8	73,9
Y	32 (43,5)	73	104	77	36	38
P	0,10 (0,14)	0,13	0,16	0,15	0,10	0,15
Mn *	0,17 (0,18)	0,50	0,69	1,43	1,41	0,004
Fe *	0,74 (0,79)	0,49	0,54	0,88	0,61	0,16

Note. 1) Numbers in brackets are recalculated as carbonate-free; 2) REE and Y content in g/ton; other elements in %.
 *Content of reactive forms of Fe and Mn extracted by repeated processing of the sample by Chester and Hughes [12] (from data in [4]).

Lithologic and mineralogic study of bottom muds along the profile, which revealed the patterns of change of sediment type forming a genetic series from shore to basin, suggests that a leading role in their formation is played by biogenic-terrigenous sediments [6]. This is shown by the strong association with land sources of the supply of both clastic and finely dispersed material, its gradational change toward the center of the ocean, and a decrease in the biogenic component with accompanying decrease in the rate of sedimentation. In the pelagic zone, where there is a diminished supply of terrigenous and ashy material from the continents, mainly introduced by the wind, there is a secondary, internal source, basaltic rocks: islands and submarine seamounts, as well as basaltic ash from volcanic islands. But the effect of these internal sources is only local in nature. With respect to the very low sedimentation rate for pelagic sediments, the hydrogenic phase, formed largely of the biota, is an important factor. Mineralogic and geochemical evidence of exhalation volcanism was found in bottom muds in the eastern part of the profile. This was limited to sediments at stations 653, 675, 655, etc., located at the intersection of the profile with the Clarion transform fault (see Fig. 1). The exhalation event is presumed to have been at the end of the Pliocene or the beginning of the Pleistocene [6]. The effect of the exhalation is barely discernible in the surface layer of sediment, and is expressed mainly as an enrichment in mobile forms of Mn and Fe.

Material for the present study was derived from samples of the surface layer (0-5 cm) of mud, brought up at 60 stations by soil tubes and bottom scoops; 51 samples of granulometric fractions (<0.001, 0.001-0.01, 0.01-0.1 mm), and of individual minerals, volcanic ash, biogenic detritus, etc. Samples were analyzed in an air-dried state. They were separated into size fractions by settling in jars. Monomineralic fractions were obtained by washing and screening and separation under a binocular microscope according to specific gravity and magnetic properties. Isolation of clay minerals from bottom muds into pure forms, without loss of adsorbed elements and with the minerals intact was accomplished with considerable painstaking work. Thus, samples were analyzed which contained other components, including

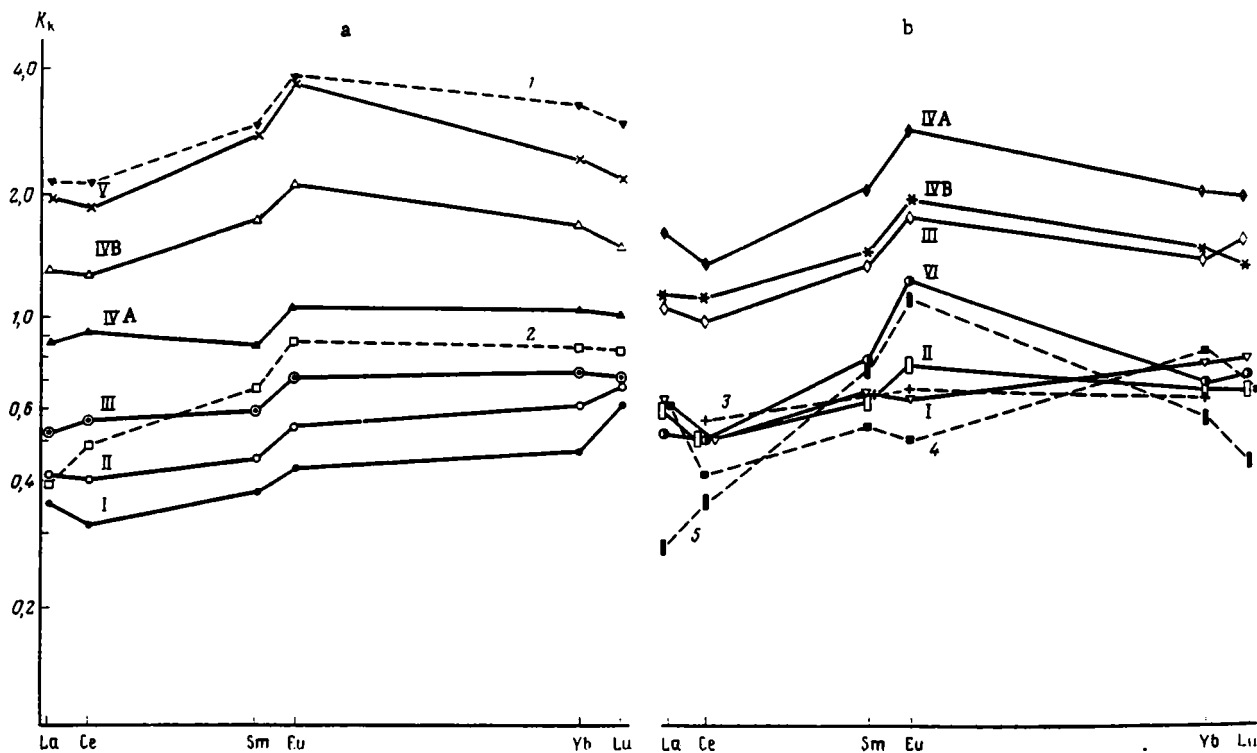


Fig. 2. Trend of REE content and composition in sediments from the margin to the center of the ocean (a, western part of profile; b, eastern part). I-VI) Lithofacies zones (zone IVB in the western part includes IVB₁ and IVB₂; in zones V and VI, as in other zones, REE content is for actual sediments). 1) Surface sediments, station 6176; 2) andesite-dacite from Hokkaido, 27 samples [15]; 3) lava, volcanic glass, and dacitic pumice (California) [11]; 4) granodiorite, southern California [8]; 5) basalt, 40 samples from six Hawaiian volcanoes [10].

hydrogenic phases, in addition to the clay minerals. The clay fraction from the profile is a mixture of several minerals with hydromica or montmorillonite predominant. They were identified by the method proposed by Biscaye [9]. The subcolloidal fraction (<0.001 mm), containing 60% or more of the clay minerals, was correspondingly called "montmorillonitic," "hydromicaceous," etc.

The REE content in the samples was determined instrumentally by neutron activation analysis. Data were obtained on six lanthanides: La, Ce, Sm, Eu, Yb, and Lu. Determinations are accurate to 10-15%. Samples were analyzed for Y by the x-ray spectral method with an analytical error of about 20%. All determinations were carried out in the laboratories of the Institute of Mineralogy, Geochemistry, and Crystallography of Trace Elements. For graphic representation of the REE composition, the method of standardization by average composition of lanthanides in clay shales was used [16]. Standardized values of REE were also used in tables for determination of the ratio of totals for several of the elements. For biogenic-terrigenous sediments of lithofacies zones V and VI, which are enriched in CaCO₃, recalculation as carbonate-free material is on the whole a more graphic comparison of the analytic data (these cases are noted in the text and tables). Associations of elements in bottom muds were determined by calculation of Spearman's rank correlation coefficient, by the "shotgun" method described in [7], and by graphic methods.

The lanthanide and Y content in sediments of the surface layer at individual stations is presented in Table 1. The average content of these elements in each lithofacies zone, along with data on P and reactive forms of Fe and Mn, calculated from material published in [4, 6], are presented in Table 2.

Effect of Continental and Island Sources of Supply on Distribution of REE in Sediments.
A graphical representation of the average REE content (Fig. 2), constructed from Table 2 and

TABLE 3. REE Composition in Various Lithofacies Zones along a Pacific Ocean Profile

Zone station	Σ REE, g/ton	Y, g/ton	La+Ce	Sm+Eu	Yb+Lu	Y, % of Σ REE + V
			% of Σ REE			
I	59.75	33	88.03	7.66	4.31	35.5
II	65.53	31	88.36	7.67	3.97	32.1
III	108.35	52.5	87.68	8.32	4.00	32.6
IVA	162.60	77	87.79	8.39	3.82	32.1
IVB	171.10	80	87.43	8.86	3.71	31.8
V	266.46	163	86.81	9.64	3.55	37.9
VI	70.44	32	85.18	10.79	4.03	31.2
IVB (sta. 6176)	298.1	160	86.88	8.85	4.26	34.9
IVA (sta. 675)	184	112	84.75	11.02	4.23	37.8

TABLE 4. Average Content of REE and Y in Nearshore (zone I) and Pelagic Clay (zone IVB) Sediments along the Entire Profile, Relative to Standard Content

Zone	La	Ce	Sm	Eu	Yb	Lu	Σ TR	Y	La+Ce	La+Ce	Sm+Eu	La/Ce
									Yb+Lu	Sm+Eu	Yb+Lu	
I	19,60	33,0	3,75	0,83	2,15	0,425	59,75	33	0,67	0,87	0,77	0,59
	32,80	55,23	6,27	1,39	3,60	0,71	100	35,57				
IVB	51,2	98,4	11,9	3,25	5,5	0,85	171,1	80	0,82	0,68	1,20	0,52
	29,92	57,51	6,96	1,90	3,21	0,5	100	31,8				
K_c	2,61	2,98	3,17	3,91	2,56	2,0	2,86	2,42				

Note. 1) Numerator, absolute content, g/ton; denominator, relative content, % (for REE, % of total of six lanthanides; for Y, % of Σ REE + Y); 2) K_c presented for lanthanides in pelagic clays; 3) La/Ce is ratio of nonstandardized content.

the literature, shows mainly that bottom muds (at least in the nearshore zone) inherit a number of significant features of REE distribution and content from denudational areas of bedrock on continents and islands. Thus, in the eastern part of the profile (see Fig. 2b) the values of these parameters in nearshore volcanic-terrigenous sediments (zone I) and hemipelagic sediments (zone II) are close to those of granodiorite from southern California [8], as well as dacitic lava, glass, and pumice from the region of the Gulf of California [11]. This situation is consistent with the conclusion, based on petrographic and mineralogical study of bottom muds in this part of the profile, that intrusive and effusive rocks of California and Mexico have a significant effect on the supply of sediments to the ocean [6].

An increase in the intermediate lanthanides, especially Eu, in the REE of Hawaiian volcanic basalts compared to the low total content [10], is also present in biogenic-terrigenous bottom muds of zone VI (see Fig. 2b), which supports the idea put forward in previous studies that these sediments were enriched by erosion of basalts and ash from volcanoes of the Hawaiian chain [6]. The similarities of REE levels between transition-type pelagic clays of zone III in the western part of the profile and andesite-rhyolite volcanics of Japan [15] is also apparent in Fig. 2a. This is in complete accord with the finding of a significant role of volcanic ash of this composition in bottom muds in this zone [6]. It must also be noted that the specific composition of lanthanides in nearshore sediments such as a deficit in Ce relative to La, acquired from erosion of rocks on land, is gradually lost with distance toward the center of the ocean. But this pattern can sometimes be seen in bottom muds as far as the zone of pelagic clays with zeolites (IVB), particularly in the eastern part of the profile (see Fig. 2b). This suggests that Ce anomalies in deep-water sediments can be partly inherited and that the magnitude of the La/Ce ratio apparently depends on allogenic components, and is not just determined by the relative amounts of authigenic phases in bottom muds [5].

Thus, the information cited above agrees closely with the concept of inheritance of the REE composition of continental and island sources by nearshore sediments. But enrichment in light and intermediate lanthanides, noted in [1], is not always the case, as can be seen

TABLE 5. Correlation Coefficient r for Elements in Sediments over the Entire Profile

Elements	r_{calc}	r_{var}	Elements	r_{calc}	r_{var}
P — ΣREE^*	0,81	0,54	Fe _{react.} — ΣREE	0,05	0,41
P — ΣREE	0,40	0,33	Fe _{tot} — Y	0,21	0,32
P — Y*	0,85	0,54	Fe _{react.} — Y*	0,25	0,56
P — Y	0,5	0,4	Fe _{react.} — Y	0,06	0,43
Mn _{tot} — ΣREE	0,49	0,27	Al — ΣREE	0,24	0,27
Mn _{react.} — ΣREE^*	0,44	0,56	Sc — ΣREE	0,25	0,27
Mn _{react.} — ΣREE	0,40	0,40	Sc — Y	0,1	0,26
Mn _{tot} — Y	0,51	0,30	Hi — ΣREE	0,1	0,27
Mn _{react.} — Y*	0,57	0,56	Ta — ΣREE	0,27	0,33
Mn _{react.} — Y	0,6	0,42	C _{org} — ΣREE	—0,51	0,27
Fe _{tot} — ΣREE	0,26	0,26	C _{org} — Y	—0,58	0,32
Fe _{react.} — ΣREE^*	0,25	0,56	CaCO ₃ + SiO ₂ amorph — REE*	—0,3	0,59

*Correlation of average content of elements by lithofacies zone (in remaining cases, relationship is for individual stations).

in Fig. 2. In every specific case the REE composition of nearshore muds will no doubt correspond to that of lanthanides of the predominant source of the sediments for that particular region of the ocean or to the total REE composition of several sources which have an effect on the sediment supply.

Trend of Changes in REE Composition with Distance from Shore. The overall trend in levels of REE and Y content and the composition of lanthanides in sediments with distance from shore, for both the western and eastern parts of the profile and for the entire profile, is shown by data presented in Tables 2-4 and Fig. 2. The marked increase in values of the intermediate REE (IREE), Sm and Eu, is sharply delineated against the background of a general increase of all REE and Y in the bottom muds (see Table 3 and Fig. 2). The data in Table 4 show that Ce content is similar to IREE. As a result of the increase in Sm, Eu, and Ce content, their role (in %) in the REE composition of pelagic clays compared to nearshore sediments increases with a decrease in the values for La, Yb, Lu, and Y (see Table 4). This is also reflected in the ratios of standardized values for light, intermediate, and heavy lanthanides in shallow-water and pelagic oozes. The preeminent increase in content of Sm, Eu, and Ce compared to other REE in deep-water sediments is also seen in coefficient of concentration (K_c) of lanthanides in pelagic clays. The REE and Y magnitudes form the following series: Eu > Sm > Ce > La > Yb > Y > Lu (see Table 4).

Thus, data obtained from an actual profile across the ocean does not support the picture of zonal REE distribution in the sediments as proposed in [1]. For example, enrichment of pelagic clays (relative to nearshore bottom muds) in heavy REE (HREE) and an increasing deficit in Ce in lanthanides with distance from shore were not found. We reported the latter observation earlier in [2]. The zonation along the profile, as shown above, appears to be the direct opposite.

The uniqueness of the sediments in the area of the Mid-Pacific submarine seamounts and the Hawaiian archipelago, located in the central part of the ocean in the region of pelagic clay deposition, affects both the level of concentration and the compositional features of lanthanides in these sediments. Sandy carbonate and clayey sediments of zone V are characterized by the highest average content of REE and Y along the profile, by a lesser role for Ce and a somewhat reduced proportion of intermediate lanthanides and Y in the REE composition relative to pelagic clays around this zone (see Tables 2 and 3). At the same time, sediments of zone V are more enriched in P (see Table 2). Meanwhile, bottom muds of the Hawaiian zone (VI) are depleted in REE and Y relative to pelagic clays (see Table 2). The amounts of Y and light REE (LREE) in the lanthanides of these sediments fall to the lowest levels found along the profile (mainly La), while the proportions of IREE and HREE increase relative to pelagic clays. The IREE here reach their highest level found in the oceanic bottom sediments studied (see Table 3). As noted above, sediments of zone VI formed to a considerable degree as products of erosion of island basalts and ash from Hawaiian volcanoes, which have the same REE ratios (see Fig. 2b).

TABLE 6. Correlation Coefficient r for Elements in Pelagic Clays (zones IVA and IVB)

Elements	r_{calc}	r_{var}	Elements	r_{calc}	r_{var}
P — Σ REE	0,97	0,65	Fe _{tot} — La	0,25	0,69
P — Ce	1,00	0,65	Fe _{tot} — Ce	0,25	0,69
P — La	1,00	0,65	Fe _{react} — Σ REE	0,43	0,69
P — Eu	1,00	0,65	Fe _{react} — Y	0,27	0,74
P — Yb	1,00	0,65	Fe _{react} + Mn _{react} — Σ REE	0,42	0,69
P — Y	0,93	0,65	Fe _{react} + Mn _{react} — Y	0,52	0,74
Mn _{tot} — Σ REE	0,53	0,56	Mn _{tot} /Fe _{tot} — La	—0,125	0,69
Mn _{tot} — Y	0,50	0,59	Mn _{tot} /Fe _{tot} — Ce	—0,125	0,69
Mn _{react} — Σ REE	0,38	0,65	Mn _{tot} /Fe _{tot} — Sm	—0,125	0,69
Mn _{react} — Y	0,38	0,69	Mn _{react} /Fe _{react} — Σ REE	0,5	0,69
Fe _{tot} — Σ REE	0,11	0,56	Fe _{react} + Mn _{react} / P — Ce	—0,5	0,69
Fe _{tot} — Yb	0	0,69			
Fe _{tot} — Sm	0	0,69			

The patterns of variation in lanthanide composition in bottom sediments along a Pacific profile, described above, are based on analysis of average values characterizing certain lithofacies zones. If the data for individual stations are examined, a more complex picture emerges. The most important of these details is the enrichment of the REE composition in Y and HREE in pelagic sediments at a number of stations. For example, the increased role of Y in lanthanides of bottom oozes at station 6176, in zone IVB₁ of the western part of the profile (see Table 3), associated with a large quantity of bony phosphate deposits, has been reported in the literature [3]. Enrichment in Y and HREE, as well as IREE, is found in the surface layer of sediments at station 675 in zone IVA, eastern part of the profile (see Table 3). Traces of hydrothermal activity have been found in the sediment section at this station [4].

The enrichment of deep-water muds in Y and heavy lanthanides, mentioned above, occurs locally and is not typical of pelagic clays of the profile as a whole (see Table 3).

What are the causes of the variations noted in levels of concentration of REE and Y and the composition of lanthanides along an actual profile of oceanic sediments? In order to answer this question, we need to examine information on the relationship of lanthanides and Y to other components of the sediment, the distribution of REE and Y by grain-size fraction of bottom muds, and the composition and quantities of these elements in minerals and individual phases in the sediments.

Relationship of REE and Y to Other Components of Bottom Mud. Examination of the relationship between components of sediment in the samples analyzed has shown that over the entire profile there is a direct relationship between the total amount of REE and Y in the bottom muds and the gross content of P and Mn. At the same time, there is no connection between lanthanides and Al, Sc, Hf, Ta, and with other components such as Fe_{tot} there is only a tendency toward a direct relationship. An inverse correlation of total REE and Y with C_{org} was found. A similar trend is seen in the relationship between lanthanides and biogenic components of the sediments such as CaCO₃ and SiO₂ (amorph.) (Table 5). A good correlation of lanthanides and Y with P has been traces not only over the profile as a whole but also in pelagic clays (zones IVA and IVB, Table 6). REE, unlike Y, is also found in bottom muds of lithofacies zones I and II. At the same time, we found no correlation of total REE and Y with Mn_{tot} and Fe_{tot} in pelagic clays, as reported in [5]. The correlations noted above for REE, as shown by selected calculations, is also generally typical of individual lanthanides, which is due to their high geochemical coherence (see Table 6). The lack of a correlation between Y and Fe_{tot} in the sediments along the profile as a whole should be noted also (see Table 5).

It has been proposed that REE and Y have a connection not with total Fe and Mn content in bottom muds, which are subject to the effect of lithogenic phases, but with their reactive forms (see Table 2), which supposedly have to a significant degree hydrogenic or hydrothermal natures and are capable of taking up lanthanides and Y from seawater [1, 5]. Specific comparisons of both average content by lithofacies zones and content at individual stations have been presented (see Tables 5 and 6). The results obtained do not confirm the hypotheses stated above. The relationship suggested occurs only for the pair Y—Mn_{react} and only over

the profile as a whole based on the content at individual stations. For total REE, only a tendency toward a connection with Mn_{react} is noted (see Table 5). No correlation is found between total REE and Y and Fe_{react} , either over the entire profile or in pelagic clays. No relationship between total reactive forms of Fe and Mn and the content of REE and Y in pelagic clays has been found, nor between the value of Mn_{react}/Fe_{react} and the lanthanide content (see Table 6). A correlation between the magnitude of $(Fe_{react} + Mn_{react})/P$ and the Ce content in pelagic clays is lacking as well, which has been reported in [5].

Thus the results of the calculations suggest that a closer connection with phosphorous and REE and Y exists in sediments of the profile. The lack of a correlation between lanthanides and Y and reactive forms of Fe and Mn in bottom muds, especially pelagic clays, may be determined by the heterogeneity and diverse origins of these forms. The amount of reactive forms of Fe and Mn, which are associated with biologic activity and probably very important in determining the REE and Y content, and possibly phosphorous as well, relative to the total amount of Fe and Mn, is apparently quite variable.

The effect of composition of oceanic sediments on the distribution of lanthanides and Y, and the conclusions drawn therefrom, will be considered in a future paper.

LITERATURE CITED

1. Yu. A. Balashov, *Geochemistry of Rare-Earth Elements* [in Russian], Nauka, Moscow (1976).
2. T. F. Boiko, N. A. Lisitsyna, G. Yu. Butuzova, et al., "Trace element hydrolyzates in sediments on a profile across the Pacific Ocean," *Litol. Polezn. Iskop.*, No. 3, 19-30 (1979).
3. I. I. Volkov and L. S. Fomina, "New data on the geochemistry of rare-earth elements in sediments of the Pacific Ocean," *Geokhimiya*, No. 11, 1603-1615 (1973).
4. É. A. Ostroumov (ed.), *Geochemistry of Diagenesis in Sediments of the Pacific Ocean (Transoceanic Profile)* [in Russian], Nauka, Moscow (1980).
5. E. G. Gurvich, V. N. Lukashin, A. P. Lisitsyn, and A. D. Kurinov, "Rare-earth elements and yttrium," in: *Geochemistry of Element Hydrolyzates* [in Russian], Nauka, Moscow (1980), pp. 71-116.
6. V. N. Kholodov (ed.), *Lithology and Geochemistry of Sediments of the Pacific Ocean (Transoceanic Profile)* [in Russian], Nauka, Moscow (1979).
7. R. L. Miller and J. S. Kahn, *Statistical Analysis in Geological Sciences*, Wiley, New York (1962).
8. L. A. Haskin, F. A. Frey, R. A. Schmidt, and R. H. Smith, "Meteoric, solar, and terrestrial rare-earth distribution," in: *Physics and Chemistry of the Earth*, Vol. 7 (1967), pp. 167-322.
9. P. E. Biscaye, "Mineralogy and sedimentation of the deep-sea sediment fine fraction in the Atlantic Ocean," *Geochim. Techn. Rept.*, 8, 12-28 (1964).
10. J. R. Budahn and R. A. Schmitt, "Petrogenetic modeling of Hawaiian tholeiitic basalts: a geochemical approach," *Geochim. Cosmochim. Acta*, 49, No. 1, 67-87 (1985).
11. K. L. Cameron and M. Cameron, "Rare-earth elements, $^{87}Sr/^{86}Sr$, and $^{143}Nd/^{144}Nd$ compositions of Cenozoic orogenic dacites from Baja California, northwestern Mexico, and adjacent West Texas: evidence for the predominance of a subcrustal component," *Contrib. Mineral. Petrol.*, 91, No. 1, 1-11 (1985).
12. R. Chester and M. I. Hughes, "A chemical technique for the separation of ferromanganese minerals, carbonate minerals, and absorbed trace elements from pelagic sediments," *Chem. Geol.*, 2, No. 3, 249-262 (1967).
13. A. J. Fleet, "Aqueous and sedimentary geochemistry of the rare-earth elements," in: *Rare-Earth Element Geochemistry*, P. Henderson (ed.), Elsevier, Amsterdam-Oxford-New York-Tokyo (1984), pp. 343-374.
14. S. E. Humphries, "The mobility of the rare-earth elements in the crust," in: *Rare-Earth Element Geochemistry*, P. Henderson (ed.), Elsevier, Amsterdam-Oxford-New York-Tokyo (1984), pp. 317-342.
15. Y. Masuda, S. Nichimura, T. Ikeda, and Y. Katsui, "Rare-earth and trace elements in the Quaternary volcanic rocks of Hokkaido, Japan," *Chem. Geol.*, 15, No. 4, 251-271 (1975).
16. D. Z. Piper, "Rare-earth elements in the sedimentary cycle: a summary," *Chem. Geol.*, 14, No. 4, 285-304 (1974).

Significant variation (in space and time) is apparent in the supply of material connected with magmatism and magmatic rocks to the ocean. In the Atlantic and Norwegian-Greenland basin, 12 large-area ash falls are distinguished. These are primarily correlated to the Northern hemisphere, which is determined to have greater "hotspot" activity due to intraplate magmatism. Three large-scale stages of the activation of such magmatism are marked to a lesser degree: late Cretaceous, Eocene, and Miocene-Recent. It is proposed that oceanic magmatism plays an important role in the supply of gas-fluid liquid material, as well as in the formation of metal-bearing sediments and sulfide deposits.

One of the first-order problems in the area of investigation of oceanic sedimentogenesis is estimating the significance of volcanic processes on the geochemical balance of sedimentation in the oceans [24]. Endogenic material has an important value in the formation of oceanic cores which by one method or another are distinguished from magmatic rocks under the ocean floor [2, 19]. Magmatic, and in particular volcanic, processes influence sedimentogenesis by supplying the ocean with gas-fluid components, solutions, and volcanoclastics. It is also necessary to consider that the magmatic rocks forming the basement of the ocean and oceanic islands disintegrate and provide a significant quantity of volcanic-terrigenous and edaphogenic products in individual regions. Geological data, and especially the results of deepwater drilling, make it possible to estimate the role of the above-named factors in the formation of the sedimentary cover in the Atlantic and Norwegian-Greenland basin.

Distribution of Volcanoclastics. Available data indicate that oceanic sediments are composed primarily of volcanogenic material of two genetic types: tephra and hyaloclastics [30]. Tephra (volcanoclastics, pyroclastics) is buried in the sedimentary cover in the form of volcanic tuffs, ash interlayers, and dispersed material. Ash interlayers, even very thin ones (fractions of centimeters) are easily distinguished in deep-water drilling cores and in geologic columns. They are generally of monomict (basaltic, rhyolitic) composition, seldom mixed. Hyaloclastics arise by underwater extrusions, including deepwater, owing to the fragmentation of the vitreous crusts of pillow lava flows. Hyalotuffs are formed at little depths as a result of phreatic-type extrusions [36]. Hyaloclastics are distributed locally in the sedimentary cover of the Atlantic and Norwegian-Greenland basin, while tephra and re-distributed volcanogenic material (tephroids) are widely distributed.

Correlation of volcanoclastic material to determined areas and epochs is observed (Fig. 1); its distribution in sections of the sedimentary cover is seen on ash-graphs (Figs. 2 and 3). Judging by the cited data, sediments are more saturated in pyroclastics in the North Atlantic and Norwegian-Greenland basin, where no fewer than 10 ash fall areas of different ages are distinguished. Only two large areas existed in the South Atlantic.

The most ancient areas of ash falls are the North American and Canarian. They are distributed almost symmetrically relative to the axis of the mid-Atlantic ridge. Ash falls here occurred from early Cretaceous to Eocene. Their greatest quantity is correlated to the late Cretaceous. In several wells (well 10), the number of volcanic ash interlayers reaches 26, and their total thickness is 10-15 m. It is necessary to note that pyroclastics from this time are strongly altered and often intermixed with zeolites.

Upper Cretaceous-Miocene ashes were observed on the highlands of the Rio-Grande and Kitov ridges. These ash fall areas are also distributed symmetrically about both sides of the mid-

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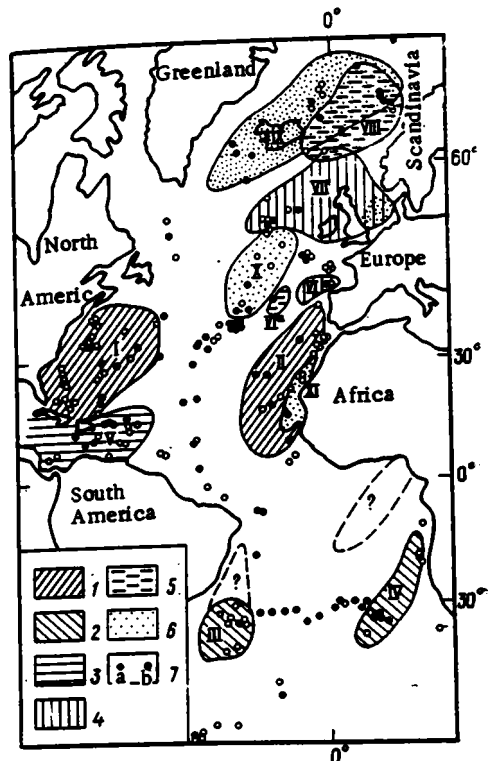


Fig. 1. Distribution of volcanic ash in areas of the Atlantic Ocean floor and the Norwegian-Greenland basin: 1-6) areas of ash falls. 1) Early Cretaceous-early Eocene; 2) late Cretaceous-early Miocene; 3) late Cretaceous-Quaternary; 4) Paleocene-Eocene; 5) Eocene-Oligocene; 6) Miocene-Quaternary; 7) deep-water drilling wells drilled to oceanic magmatic basement (a) and halted in sedimentary cover (b); I-XI) numbers of the ash fall areas. Dots delineate areas of proposed large-scale ash falls.

Atlantic ridge. On the Kitov ridge, late Cretaceous and Eocene ash falls are most abundant. The tuff thickness here reaches several tens of meters (wells 524 and 359). After a prolonged lull, ash falls recommenced in the early Miocene, centering on the northern part of the ridge (well 530). On the Rio-Grande highland, abundant ash falls with a total thickness of interlayers up to 30 m (well 516) occurred in the Eocene and early Miocene. An insignificant quantity of volcanic ash was deposited in the middle Pliocene (well 356).

Ash falls occurred over a long time, from the late Cretaceous (and possibly also earlier) to the Recent period in the Caribbean basin and in the region of the Lesser Antilles island arc. The number of ash interlayers in separate wells (wells 146-154) reaches 40-85, and the total thickness is tens of meters. It is characteristic that the ash fall areas are younger (Oligocene-Recent) and less extensive on the Atlantic side of the arc than on the Caribbean side. Using this fact, for a condition of equal separation of ash on both sides of the arc, it is possible to determine the size of the subblast area of oceanic lithosphere of Atlantic.

Paleocene-Eocene ash falls were observed in the northwestern part of the North Atlantic. They encompass the Rockall highlands and the Faroe-Icelandic threshold. Synchronous thick accumulations of volcanic ash and tuffs were observed in the North Sea [37]. Ash falls were particularly thick in the southwestern part of the Rockall highlands. The thickness of the terrigenous-pyroclastic and tephroidal deposits of the upper Paleocene-lower Eocene reaches 600-700 m here (well 555). The pyroclastic composition is alkaline-basaltic, and rhyolitic ash is present [35]. The accumulation of ash horizons occurred in conditions of underwater deltas, moving coastal-oceanic shallow water, and in zones of relatively deep oceanic water. An insignificant area of Paleocene-Eocene ash is noted in the Bay of Biscay (wells 118, 119).

Eocene ash falls occurred in the Norwegian Sea and in the western European trough. The thickness of volcanoclastic interlayers in separate wells is equal to 10 m (well 608). These layers adjoin Paleocene-Eocene ash layers and partially cover them (see Fig. 1); and, in their turn, they are covered by Miocene-Quaternary ash layers. The latter are concentrated in three main regions: Iceland, the Azores, and Cape Verde. In addition, a series of small Miocene-Quaternary areas exist (Guinea, Tristan, etc.) which is connected with regions of island intraplate vulcanism; however, there are no data on the distribution of pyroclastics in sections of sedimentary sequences close to these regions. Miocene-Quaternary volcanism on the islands is characterized by high explosivity. Thus, from data of drilling 1000-m wells on

Fig. 2. Distribution of interlayers of volcanic ash and dispersed pyroclastics in Cenozoic deposits of the Norwegian-Greenland basin: 1-3) interlayers of volcanic ash, tuff (1) basic composition; 2) acid; 3) mixed; 4) volcanic basic glass, palagonite, ash dispersed in the sediments; 5) the same, together with acid volcanic glass; 6) zeolites in sediments; 7) interruptions in sediment accumulation; 8) intervals in drilling in which data are absent; 9) wells left in basalt; 10) the same in sediments. The numbers on the figure are the well numbers. Nor. tr.) Norwegian trough; Ice. plat.) Icelandic plateau; Knip. rid.) Knipovich ridge; Ice. plat.) Icelandic plateau.

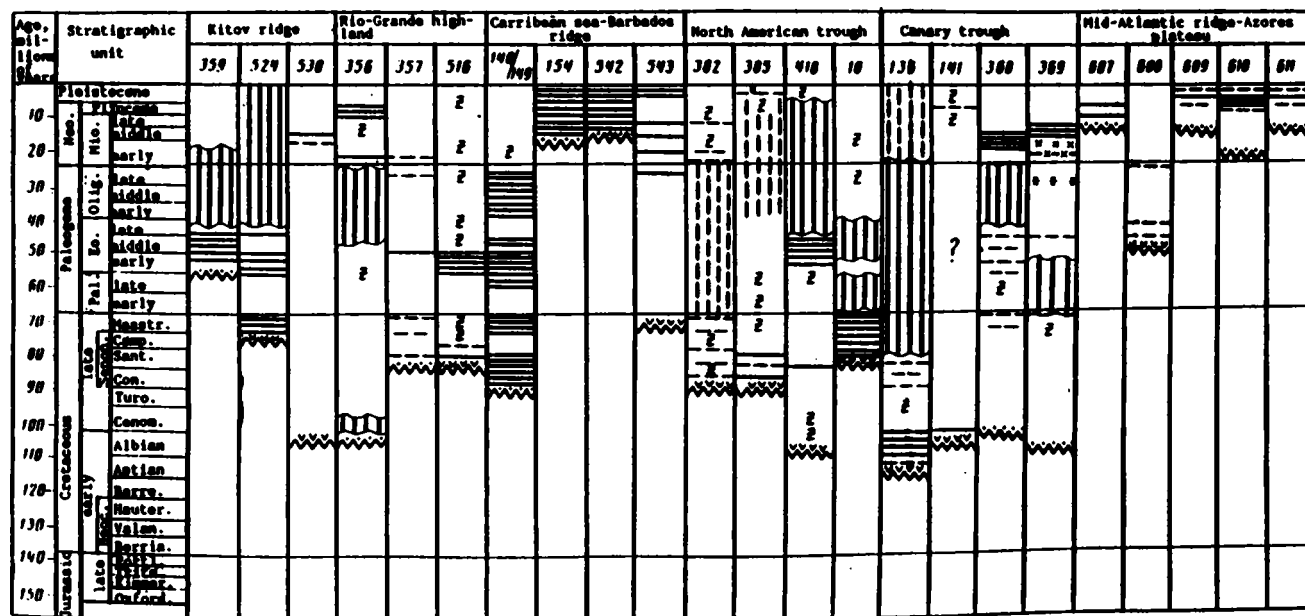


Fig. 3. Distribution of interlayers of volcanic ash and dispersed pyroclastics in Mesozoic and Cenozoic deposits of the Atlantic Ocean. Legend as in Fig. 2. Maastr.) Maastrichtian; Camp.) Campanian; Sant.) Santonian; Con.) Coniacian; Turo.) Turonian; Cenom.) Cenomanian; Barre.) Barremian; Hauter.) Hauterivian; Valan.) Valanginian; Berria.) Berriasian; Portl.) Portlandian; Titn.) Tittonian; Kimmer.) Kimmeridgian; Oxford.) Oxfordian; Neo.) Neogene; Pal.) Paleocene; Eo.) Eocene; Olig.) Oligocene; Mio.) Miocene.

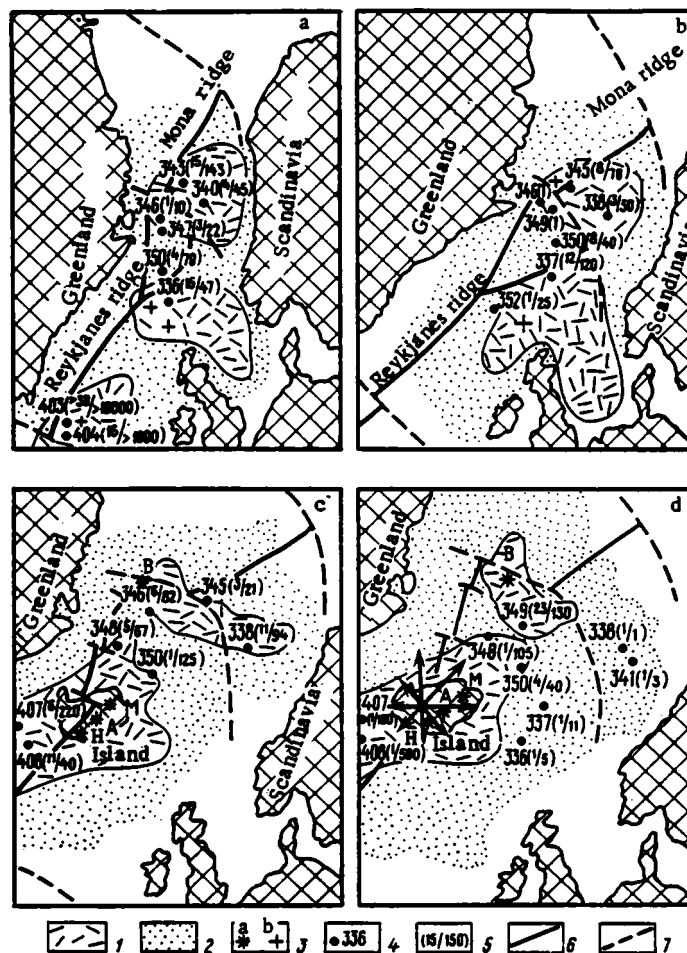


Fig. 4. Areal distribution of volcanic ash interlayers in different epochs of the Cenozoic (a, Eocene; b, Oligocene; c, Miocene; d, Pleistocene) dependent on the position of active island volcanoes in the Iceland region. 1, 2) Areas with ash falls (1, strong; 2, weak); 3) volcanoes (a, known; b, presumed); 4) deep water drilling well and its number; 5) in the numerator, the number of ash interlayers; in the denominator, their total thickness, cm; 6) rift zones and the axis of the active mid-ocean ridge; 7) zones of transform faulting. Shown in the Pleistocene scheme is a contemporary rose-diagram of winds above Reykjanes (Iceland) at a height of 9 km (compiled by R. V. Abramov). Volcanoes: A) Askja; H) Hekla; M) Mivatte; B) Beerenberg.

the island of San Miguel (Azores), nearly 60% of the section is composed of the products of explosions [42]. In Iceland tuffs occur in wells at depths up to 2 km. The coefficient of explosivity of shallow water volcanos (Surtsey, Kapil'inish) reaches 0.7. Over a short time period (1963-1966), the underwater volcano Surtsey (Reykjanes ridge, Iceland) erupted nearly 0.7 km³ of ash and 0.3 km³ of lava into the ocean, forming an island. The large volcanic cones on many islands (Teide volcano, 3.7 km; Berenberg volcano, 2.5 km) attest to the great explosivity. A significant part of the volcanic ash fell into the ocean from the island eruptions, and it was distributed there in agreement with existing currents and winds [10]. The effect of island volcanism is clearly seen, for example in the Iceland region (Fig. 4). Beginning with the Miocene, when Iceland appeared, distribution of volcanoclastics in the sediments may be connected with the activity of volcanoes located on this island. It is more likely that other volcanoes acted in the Eocene and Oligocene.

Volcanoclastic distribution is uneven both in space and time (see Figs. 2 and 3). The following main aspects of volcanoclastic distribution in the stratigraphic sections are apparent: 1) correlation to the base of sedimentary cover; 2) "continuous" distribution of

TABLE 1. Quantity of Pyroclastics Buried in the Atlantic and Norwegian-Greenland Basins

Area number	Area	Age	Distribution area, km ²	Average total thickness of volcanoclastic	Volume, km ³
I	North America	Cretaceous-Eocene	600	3	1800
II	Canary	Cretaceous-Eocene	600	3	1800
III	Rio-Grande	Cretaceous-Miocene	100	10	1000
IV	Kitov	Cretaceous-Miocene	200	20	4000
V	Caribbean-Lesser Antilles	Cretaceous-Recent	500	10	5000
VI	Biscay and Western Europe	Paleocene-Eocene	100	3	300
VII	Rockall and North Sea	Paleocene-Eocene	600	15	9000
VIII	Norwegian	Eocene-Paleocene	500	20*	10,000
IX	Iceland	Miocene-Recent	800	40*	32,000
X	Azores	Miocene-Recent	200	100*	20,000

*Dispersed pyroclastics are considered in addition to the interlayers.

volcaniclastics in sedimentary cover; 3) discontinuity in the position of horizons and layers of volcanoclastics in sections of sedimentary sequences. The first aspect is characteristic of the most ancient areas, where pyroclastics are primarily correlated to upper Cretaceous (North American, Canary, Kitov areas) and upper Paleocene-early Eocene (Rockall, Biscay areas) deposits; the second aspect is characteristic of areas adjoining islands of the Lesser Antilles arc and to a small degree for the Iceland and Azores areas, where, beginning with Miocene, frequent repetition of pyroclastic interlayers in the sedimentary cover is observed; and the third aspect is characteristic of the Norwegian and Canary-Cape Verde areas and the Rio Grande highland.

Definite regularities are seen in the distribution of ash falls by area and their alternation in time. A high symmetry of areas relative to the axial line of the mid-Atlantic ridge is characteristic of the most ancient (Cretaceous) ash falls. Cenozoic ash falls are asymmetrically arranged and are largely correlated to the Northern hemisphere. Migration of these areas from the boundaries of the European continent to the axial zone of the mid-Atlantic ridge is observed; that is, the more ancient areas lie to the east and the younger to the west, close to the ridge or on the ridge (see Fig. 1). Such regularity in the migration may be explained by the input of pyroclastic material from relatively immobile and periodically active eruptive volcanic centers on the eastwardly moving plate. Such volcanic centers (hot spots) for areas VII, VIII, and IX (see Fig. 1) may lie on the Reykjanes ridge and in Iceland, while for areas VI, VI-a, and X they are on the Azores plateau.

Only an approximate quantitative estimate of the volumes of pyroclastics within the limits of the main Meso-Cenozoic areas of ash falls in the Atlantic and Norwegian-Greenland basins (Table 1) is possible due to deficient data. We note that the calculated volume is somewhat understated, particularly in ancient Mesozoic and Paleogene ash falls, the products of which are strongly altered and transformed into zeolites and other minerals, and not considered in the computed volumes. It is also difficult to study dispersed pyroclastics in ancient ashfalls, since they are likewise generally transformed and with difficulty amenable to diagnostics.

Estimation of the total volume of volcanoclastics located in different stratigraphic intervals of the sedimentary cover of the Atlantic and Norwegian-Greenland basin indicates the unevenness of its distribution in time. Three main intervals are distinguished in which almost the entire volume of volcanoclastics is concentrated, while the total duration of these intervals only reaches nearly 40% of the time for formation of the sedimentary cover. The greatest (~60%) quantity of volcanoclastics is concentrated in the Miocene-Recent interval, subsequently followed by the lower Eocene-upper Paleocene and upper Cretaceous intervals, to which each contribute 15-20% of the entire volume of pyroclastics. The gaps between the named intervals are poor in volcanoclastics.

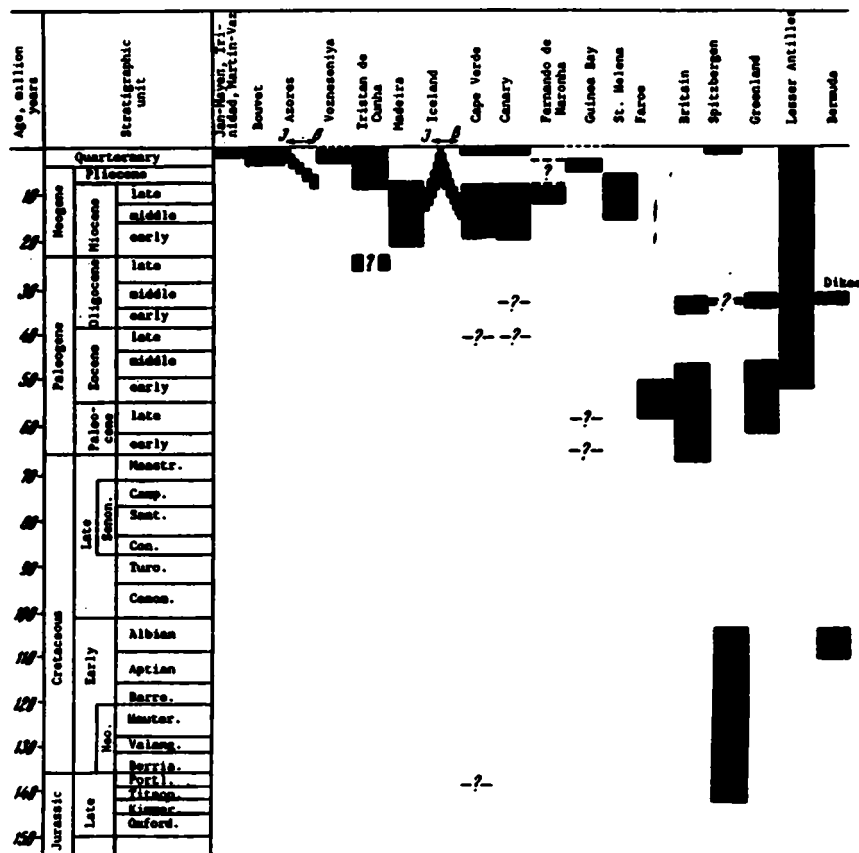


Fig. 5. Age of magmatic rocks developed on islands of the Atlantic Ocean and Norwegian-Greenland basin. Question marks denote uncertain data. See Fig. 3 caption for abbreviations.

The main intervals distinguished in the sedimentary cover which are enriched in volcanoclastics are composed of a series of finer intervals in different regions, reflecting epochs of strengthening in intraplate eruptive volcanism. Thus, in the Miocene-Recent interval it is possible to distinguish early Miocene, middle Pliocene, and Pleistocene epochs, which correspond to epochs of a global increase in explosive vulcanism [16, 38]. It is interesting to compare data on the distribution of volumes of pyroclastics in time with data on the ages of magmatic rocks on islands in the Atlantic and Norwegian-Greenland basin (Fig. 5). As we see, the Miocene-Quaternary magmatic epoch on the islands is the interval of the greatest quantity of volcanoclastics in the sedimentary cover. It is also possible to note a relatively early Eocene-late Paleocene epoch. The late Cretaceous magmatic epoch is not represented on the islands, while it is reflected in the increased quantity of volcanoclastics in the sedimentary cover. This inconsistency is possibly explained by the fact that upper Cretaceous magmatic rocks on the islands are buried to a significant depth and have not yet been studied.

Volcanoterrigenous material is represented in the sedimentary cover from dry land as a result of the disintegration of volcanic rocks. The main mass of it enters from the islands, and it is added to by rocks of the alkaline-basalt series. Estimates of volumes of material found in the sedimentary cover of the Atlantic and Norwegian-Greenland basin have not been carried out up to this time. Meanwhile, there is a basis to assume that in some regions of the ocean it is extremely significant. It is possible to show this from the example of the Icelandic trough. The emergence of Iceland caused an increase in the sedimentation rate of several times in the Icelandic trough [27]. The sediment composition was strongly altered: instead of carbonates they became greywacke. The volcanoterrigenous material of Iceland entered the trough particularly intensively in the Pleistocene, and it enters at the present time. Its greatest quantity is delivered from an island onto the shelf by temporary flows (Jokulhla Upami, arising from breaching of glacial lakes and by subice volcanic eruptions [10]). Shelf sediments were formed owing to volcanoterrigenous and teph-

roidal material around Iceland. Faulting of the material from the shelf into the adjacent trough occurred with the achievement of some thickness and a critical slope angle where the material was distributed over significant areas. Only during Quaternary time in the southern part of the Icelandic trough, a thick (>200 m) sequence of volcanoterrigenous sediments was deposited. They were carried out from Iceland, and cover roughly over 1000 km (well 115). The volume of material carried into the trough in the Pleistocene reached no less than 100,000 km³, and its total quantity entering the Icelandic trough since the Miocene, when Iceland emerged, was apparently 3-4 times greater. A significant volume of volcanoterrigenous material was carried out from Iceland to the Icelandic plateau. The thickness of the sedimentary cover here, from NSP data, exceeds 1.5 km [7]. Other sources of sedimentary material input onto this plateau were practically nonexistent. The volume of material input to the plateau from Iceland is estimated to 30,000-50,000 km³. The total volume of volcanoterrigenous material buried in sedimentary cover as a result of disintegration of Icelandic volcanic and volcanoclastic rocks apparently reaches 400,000-500,000 km³, that is, almost equal to the Recent volume of this volcanic uplift.

It is possible to propose that volcanoterrigenous material has more value in the structure of the sedimentary cover in regions of other large-scale volcanic uplifts such as the Azores plateau, Sierra Leone highlands, Rio Grande, Cape Verde island, and the Kitov ridge.

Obtained data show that edaphogenic material formed due to disintegration of crustal rocks of the oceanic floor has great value in the structure of sedimentary sequences which lie in the channel zones of transform faults. Thus, in the channel of the Romanche fracture, deep seismic probing distinguished a sequence composed of three layers with thicknesses of 1, 2, and 3-4 m, with velocities of 2, 3.4, and 4.3 km/sec, respectively [8, 22]. Judging by dredge data, edaphogenic rocks, represented by serpentinitic gravelites, sandstones, and siltstones of varying degrees of lithification also occur in the Romanche channel, along with fragments of basite-hyperbasite magmatic rocks [1, 6, 29]. Apparently, they also fill channels in the Romanche fracture. The great thickness of these deposits is explained by tectonic and geomorphological features of fractures: first, by their great heights and steep sides; second, by the great tectonic activity of the fracture and by the duration of differently oriented shear deformations of the southern and northern blocks of the earth's crust; third, by the existence here of avalanche-type sedimentation [20]. A great quantity of breccias and mylonites of peridotitic, serpentinitic, and basaltic composition is formed as a result of active tectonic motions in the fracture. Under the influence of its inherent weight and earthquakes, these materials, along with biogenic sediments, are transported to the bottom of the channel, buried, compacted, and lithified there. The channel floor experiences isostatic downwarping, compensating for the accumulation of new portions of sediments. The total thickness of the sediment sequence, and in particular edaphogenic sediments, in the channel of the Romanche fracture, judging by geophysical data, is equal to 6-7 km, the volume is nearly 30,000 km³, and the weight is nearly $6 \cdot 10^{13}$ tons, which many times exceeds the annual solid runoff from dry land into the Atlantic Ocean, which reaches nearly $2.8 \cdot 10^6$ tons/yr.

An increased sedimentation rate and thickness of sedimentary cover are also noted in other transform fracture zones (Vina, Charlie Gibbs, Jan-Mayen), in the channels of which sediments with a high content of edaphogenic material, breccia, and basalt mylonites are found [10]. In one zone of the Southern Atlantic fracture (30° S lat.) we determined that Recent transport of edaphogenic material (fragments of serpentinites up to 5 cm in size) exceeds several kilometers. Some rounding of fragmental material occurred due to this. In more ancient periods, when the channel began to be filled, transport of material may have reached tens of kilometers, and rounding was more significant. It is proposed that these positions explain the presence of rather thick horizons of basaltic sands, gravels, and sandstones amid bedding of pillow lavas. In some wells (for example well 396B) their thickness reaches more than 60-70 m. Most likely this is edaphogenic material transported downward along the slope of the ridge into the rift valley.

Thus, the sequence of edaphogenic sediments formed as a result of the disintegration of magmatic rocks on the ocean bottom may have significant thickness (tens, hundreds, and even thousands of meters).

Gas-fluid and liquid products of oceanic magmatism and volcanism are delivered to the ocean and sedimentary cover almost without "loss," while in subaerial volcanism they (particularly gas products) escape into the atmosphere to a significant degree. Underwater

basalts of the Atlantic and Norwegian-Greenland basin, shown by direct measurements, are characterized by high gas contents, measured from a few units to tens of millimeters in 1 g of rock [17], which is 2-3 times greater than from Icelandic basalts. In the composition of the gas-fluid phase in underwater basalts are noted H_2O , CO_2 , CO , CH_4 , H_2 , N_2Cl , B , He , heavy hydrocarbons, and other gases. Correlations between H_2 and H_2O give a basis to the proposal that H_2O is a product of the oxidation of mantle hydrogen to a significant degree. Apparently, a series of other gases is also abyssal. A higher value of CO_2/H_2O is characteristic for oceanic basalts in comparison with island arc magmas. On the basis of tests it is found that basaltic melts may dissolve up to 8-10% water at depths of magma formation and at depths of magmatic chambers (at depths of 30 km and more) [15]. The solubility of CO_2 in silicate melts only reaches 0.18% for a pressure of 10 kbar. The presence of CO_2 significantly decreases the solubility of H_2O . With the rise of the melt into a region with lower pressure, the gas component is gradually segregated. It rarely effervesces and forms porous basalt with eruption of magma onto the surface of the ocean bottom. Magma may also effervesce in the supply channel if the partial pressure of dissolved gases exceeds the external pressure, which occurs in places of channel constrictions and fractures, where the flow rate of the magma increases. A series of other facts attest to the existence of gas-fluid flow, in addition to data on the porosity and gas permeability of basalts. These are: 1) the presence of pegmatoidal structures and water containing magmatic minerals in gabbroids and ultrabasic rocks; 2) the presence of microinclusions of acid glass in basalts; 3) cases of pyroxene-plagioclase fractionation of tholeiitic magma; 4) direct measurement of gases and fluids in basalts. Petrological evidence on the "dryness" of basaltic magma in oceans, as well as on continents, from experimental data and the composition of mineral inclusions may be explained by the following causes: 1) the high degree of openness of the system in which the generation and evolution of basalts occurs; 2) the predominance of CO_2 over H_2 in the composition of the gas-fluid phase; 3) the insignificant (less than 0.5 weight %) content of gas-fluid phases in magma, which does not influence the fractionation order of crystals. Other causes that remain unclear for the present are also possible. These determine the evolution of basaltic magma on the "dry" path, even with the presence of a sufficiently large gas-fluid flow.

Data on basalt porosities may roughly indicate the quantity of gases and fluids segregating from the magma into the ocean. Multiple measurements in deepwater-well cores show that its value varies within wide limits from 2 to 30%. The average value of porosity in Atlantic basalts is nearly 6.5%. On the basis of this, it is possible to find the approximate quantity of gases and fluids segregating from basalts. Their annual supply into the ocean reaches $M_{f1} = 0.325 (V \cdot P) / 100 = 3.6 \cdot 10^{14}$ g/yr (where 0.325 is the critical density of fluid, taken from water; V is the volume of the basaltic crust forming in the area of mid-ocean ridges; P is the average porosity of basalts in the core from the deepwater drilling well, equal to 6.5%). By Lisitsyn's computation [18], nearly $6 \cdot 10^{16}$ g of basaltic material formed annually in the oceans, which with an average density of 2.88 g/cm^3 , reaches a volume of $2.1 \cdot 10^{16} \text{ cm}^3/\text{yr}$. It is necessary to consider the resultant quantity of gases and fluids ($3.6 \cdot 10^{14}$ g/yr or 350 million tons/yr) as a minimal background value. These gases and fluids are separated from the basalts over a large area in active zones of mid-ocean ridges and are dispersed in the ocean and sedimentary cover.

Geological and experimental data attest to the important role of melt fluids in the formation of hydrothermal occurrences, possibly including oceanic sulfide ores [4]. The extracting power of fluids is increased many times, if even small quantities of salts are present in them (fractions of percents of halides, carbonates). They are enriched by ore elements (up to tens of grams per liter) and become hydrothermal brines. It is entirely possible to postulate the formation of hydrothermal brine due not only to mantle fluids, but also the inflow of marine water in conditions of oceanic magmatism, for small depths of magmatic chamber occurrences. Observations from manned underwater apparatus show that concentrated gas-fluid and hydrothermal currents exist on the ocean bottom ("black and white smokers"), due to which sulfide and sulfate tubular bodies and other ore deposits are formed. Direct quantitative estimation of ore components in the gas-fluid constituents which are carried out into the ocean in such currents is difficult to perform, since this requires extremely detailed exploration-investigative efforts at great depths. However, indirect estimate of material carried out from the magmatic source in the gas-fluid phase may be done by the following means. It is known that oceanic basalts and gabbroids are comagmatic, that is, they arise from magma of a single composition. Moreover, data show that there are differences between the chemical compositions of basalts and gabbroids in the series of rock-forming oxides and small elements. This is indicated by both the average composition of the indicated rocks,

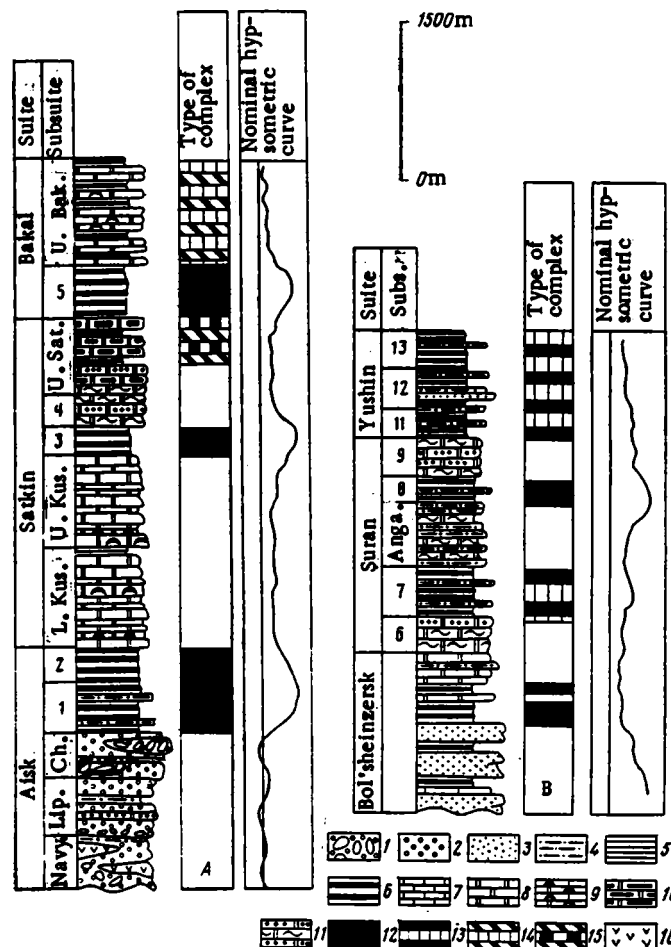


Fig. 1. Occurrence levels and types of carbonaceous sediments in the Lower Riphean of the Bashkirian meganticlinorium (A - northern areas, B - central areas): 1) conglomerate; 2) medium- to coarse-grained sandstone; 3) fine-grained sandstone; 4) siltstone; 5) clayey schist; 6) coaly-clayey schist; 7) limestone; 8) stromatolitic limestone and dolomite; 10) coaly-clayey dolomite; 11) dolomite with silt-clay impurities; 12-15) types of carbonaceous complexes (12 - of marine genesis, type I, 13 - shallow-sea genesis associated with terrigenous formations, type IIa, 14 - shallow-sea genesis associated with carbonate formations, type IIb, 15 - coal-clay dolomites in association with carbonaceous schists, type III); 16) basic, effusive and subvolcanic rocks. Numbers in the columns indicate subsuites: 1) Kisezan; 2) Sungur; 3) Polovinkin; 4) Nizhnesatkin; 5) Makarov; 6) Min'yak; 7) Berdagulov; 8) Serdauk; 9) Lapyshtin; 11) Vyazov; 12) Bagaryshtin; 13) Sukhin.

The overlying largely sandy beds of the Lipov subsuite of the Aisk suite were formed in alluvial-deltaic environments. Various types of middle-sized to small oblique linear and leveling unidirectional stratification with indistinct rhythmic material sorting in small layers is observed in the sandstones of this location; small-pebble conglomerates and gritstones are found at the base of obliquely stratified members. They cut slightly across the subjacent sediments. There are stream ripple signs and other textures. According to Garan' [6], intraformational washout traces can be observed at the bottom of the Aisk suite, indicating a local restructuring and the disappearance of selected coarse-clastic members from the section.

The overlying Lipov sandstones of the Chudinsk subsuite consist of members with alternation of sandstone, siltstone, and clay schist, often with lenses and pockets of gravel matter, and relatively thick (up to 50-70 m) elongate lenses of poorly sorted conglomerates and conglomerate-breccias with micaceous matrix; apparently, these are deluvial-proluvial formations that have undergone partial reworking in a marine environment.

TABLE 2. Average Rock Composition, weight %

Rocks	SiO ₂	TiO ₂	Al ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	P ₂ O ₅	Literature source
Oceanic gabbroids	48,03	1,06	16,49	8,68	0,14	8,98	11,06	2,60	0,25	0,07	[12]
Basalts (MOR)*	49,81	1,43	16,01	11,49	0,18	7,84	11,32	2,78	0,22	0,14	[11]
The same	49,14	1,17	15,64	9,04	0,16	8,22	11,84	2,40	0,20	0,12	[43]
Basaltic glass (MOR)*	50,53	1,56	15,27	10,46	—	7,47	11,49	2,62	0,16	0,13	[39]
Gabbro (well 334)†	50,69	0,42	16,22	7,28	0,14	9,81	13,43	1,39	0,11	—	[33]
Type 1 basalts (well 334)	50,87	0,75	15,00	8,89	0,17	8,37	12,94	1,76	0,17	—	[34]

*MOR: mid-ocean ridge.

†Well 334; mid-Atlantic ridge.

TABLE 3. Carrying Out of Metals and Other Elements from Oceanic Gabbroids

Indicator	Fe	Mn	V	Cu
Av. content in basalts and glasses of ocean,* weight %	8,15	0,154	0,0190	0,0097
Av. content in gabbroids of ocean,* weight %	6,95	0,108	0,0138	0,0086
Difference between contents in basalts and gabbro, weight %	1,20	0,046	0,0052	0,0011
Carrying out of elements from gabbro intrusions,† g/yr (in million tons)	$3,6 \cdot 10^{14}$ (360)	$1,14 \cdot 10^{13}$ (14)	$1,7 \cdot 10^{12}$ (1,7)	$3,3 \cdot 10^{11}$ (0,33)
Indicator	Zn	Ba	P	F
Av. content in oceanic basalts and glasses,* weight 5 %	0,0063	0,0062	0,03	0,02
Av. content in oceanic gabbroids,* weight %	0,0055	0,0031	0,01	0,005
Difference between contents in basalts and gabbros, weight %	0,0008	0,0031	0,02	0,015
g/yr (in million tons)	$2,4 \cdot 10^{11}$ (0,24)	$9,3 \cdot 10^{11}$ (0,93)	$6 \cdot 10^{12}$ (6)	$4,5 \cdot 10^{12}$ (4,5)

*Data adopted from [11, 12, 31, 33, 44].

†Mass of gabbro is taken as equal to 1/2 the mass of basalts generated in middle ridges of ocean, that is, $3 \cdot 10^{16}$ g/yr.

which is calculated for all oceans, and in regional data (Table 2). As seen, the average composition of oceanic gabbro is significantly distinguished from the average composition of basalt (tholeiite), by smaller contents of TiO₂, FeO, MnO, and SiO₂. Differences in the components of other oxides are insignificant. The indicated variation in composition may arise after emission of the basalts from the magmatic chamber as a result of variation in the remaining melt. In view of their rapid extrusion and crystallization, basalts vary less, and better reflect the composition of the initial melt than gabbroids, which exist in a melted state for a longer time and are subjected to differentiation and gas-fluid reworking. Basaltic glasses are closest in composition to the initial melt [39].

Products of fractional differentiation of the melt remain in the magmatic chamber, and they are consequently considered in the calculation of the average composition of gabbro. Gas-fluid reworking of the melt leads to the carrying out of a series of components from the magmatic chamber, including the above-noted rock-forming oxides and series of ore elements (Table 3). Knowing the variation between the composition of basalts and gabbroids, as well as the mass of the gabbroids, it is possible to estimate the quantity of material carried out from this mass. Nearly $6 \cdot 10^{16}$ g (60 billion tons) of basaltic material is formed in the oceans annually, going to the formation of the earth's crust [18]. We will consider that half of this mass belongs to intrusions of gabbroids. The average content of iron reaches 6.95% in gabbroids, while in basaltic glasses it reaches 8.15% (see Tables 2 and 3). We pro-

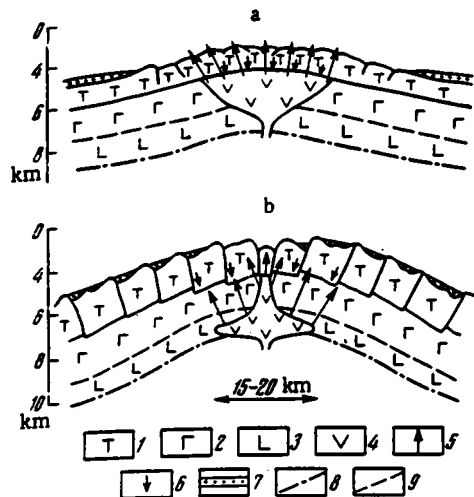


Fig. 6. Principal scheme of the entrance of ore components into the gas-fluid phase from magmatic sources under mid-ocean ridges. a) Ridge with rapid spreading rate (East Pacific rise); b) ridge with slow spreading rate (mid-Atlantic ridge and others): 1) basalt layer; 2) gabbro; 3) cumulate series; 4) magmatic source; 5) gas-fluid output from the magmatic source; 6) entrance of marine water into the earth's crust; 7) sediments; 8, 9) boundaries (8, Mohorovicic; 9, isotropic gabbro and cumulate series).

pose that gabbroids lost 1.2% of iron as a result of more prolonged working by transmagnetic fluids in comparison with basalts. In every layer of gabbroids generated under the mid-ocean ridges over 1 year ($3 \cdot 10^{16}$ g/yr), iron losses reach $(1.2 \cdot 3 \cdot 10^{16})/100 = 3.6 \cdot 10^{14}$ or nearly 360 million tons/yr. Losses of Mn, V, Cu, Zn, Ba, and F (see Table 3) are determined by similar estimation. The carrying out of chemical elements by melt gases and fluids occurs not only from gabbro intrusions. It apparently also proceeds from the asthenosphere, where partial melting of the mantle substrate is observed, and from deeper layers experiencing degassing. As is known, the main mass of vapors and gases in the earth's atmosphere occurred through degassing of the volatile fraction of mantle [3].

Chemical elements are carried out by complicated means from the depths of the earth into the ocean. Interaction of gases and magma is one of the steps of this process [21]. The trial undertaken above of a quantitative estimate of a similar interaction of a gas-fluid phase with a tholeiite magma in sources of gabbroid formation is only a first approximation to actual understanding of the given process.

It is noted that the volume of endogenic output of ore elements into the ocean at mid-ocean ridges depends on the spreading rate. Formation of large volumes of metal-bearing sediments is observed in the eastern part of the Pacific Ocean, where the spreading rate reaches 8-12 cm/yr. The dependence of output on the spreading rate may be explained as follows: that high-velocity ridges are distinguished from low-velocity ridges by the form of their magmatic chambers, by their greater volume and smaller depth of deposition of the chamber surfaces from the surface of ocean floor (Fig. 6) [14, 40]. The thickness of the basaltic layer has an important value, since it is 1.5-2 times greater on low-velocity ridges (mid-Atlantic and others) than on high-velocity ridges (East Pacific rise) [22]. All these features of high-velocity ridges assist both in the easier penetration of marine water into the magmatic chamber, and the more complete recovery of the melt gas-fluid phase into the hydrothermal system of the ridges. At low-velocity ridges, the volatile components which are segregating from the magma are dispersed to a significant degree in the basaltic layer (see Fig. 6).

The Atlantic ridge is a region of ocean with a low spreading rate. Here, each kilometer of the mid-ocean ridge generates two times less basalt than the oceanic average, and six times less than in the East Pacific rise. Conditions for the formation of extensive magmatic chambers of shallow depth are seldom created here. Gabbros arise even in the rift zone, undergo metamorphism, are deformed, and often are brought out in the form of discreet fragments on the surface of the ocean floor. Existing gas-fluid flow (indicated by amphibolization of gabbroids, pegmatoid structures, porosity of basalts, and other data), is probably of little thickness. In samples of gabbroids obtained on a series of portions of the mid-Atlantic ridge, the ore element content was less than in basalts. This indicates the presence of gas-fluid output from the magmatic chamber, which is confirmed by the locations of metal-bearing sediments and mineralized zones, generally small in scale.

We do not present the question of the formation of oceanic metal-bearing sediments and sulfide ores due to the carrying out of ore elements by processes of the interaction of basaltic basalts with marine water as simply as it is proposed by many investigators, based on

the results of experiments [32, 41]. Geological data indicate that, for these processes, the larger part is formed of Fe-Mg smectites and altered basalts enriched by ore components [13, 25, 26, 28]. Therefore, it is possible to propose that the carrying out of ore components goes from deeper horizons of the earth's crust or from a magmatic source.

On the basis of the discussion it is possible to draw the following conclusions.

1. The role of oceanic magmatism and magmatic rocks in the supply of material for sedimentogenesis and ore genesis in the ocean is distinguished by significant variation in space and in time.

2. Great quantities of pyroclastics enter the ocean only in discreet regions. A clear asymmetry is observed in the Atlantic in the distribution of these products in the Mesozoic sediment cover, and their predominant correlation to the Northern hemisphere and eastern part of the ocean, which is probably caused by the greater activity of "hotspots" of intraplate volcanism. In the history of the Atlantic, three large-scale stages of such activation are noted to a lesser degree: late Cretaceous, Eocene, and Miocene-Recent. Nearly 80-90% of the volume of all pyroclastics buried in the sedimentary cover of the Atlantic Ocean and Norwegian-Greenland basin is connected with them.

3. Solid products of the mechanical disintegration of oceanic and island magmatic rocks are not only correlated to the base of the sedimentary cover, but also add thick sequences in individual troughs (Icelandic and others), where they entered as a result of avalanche drift from shallow water portions. Possible coarse (thickness in hundreds of meters) bodies of edaphogenic sediments are found in the channels of several transform fault zones (Romanche, Charlie Gibbs, Jan-Mayen).

4. Taking into account the porosity of oceanic basalts and other data, it is possible to propose that oceanic magmatism plays an important role in the supply of gas-fluid and liquid material, as well as in the formation of metal-bearing sediments and sulfide deposits.

LITERATURE CITED

1. Yu. A. Bogdanov and V. V. Ploshko, "Gabbro-peridotite formation of the Romanche depression (Atlantic Ocean)," *Dokl. Akad. Nauk SSSR*, 201, No. 6, 1453-1457 (1971).
2. G. Yu. Butuzova, "On the question of sources of material in hydrothermal-sedimentary oceanic ore genesis," *Litol. Polezn. Iskop.*, No. 5, 3-18 (1986).
3. A. P. Vinogradov, *Gas Regime of the Earth/Chemical Regime of the Earth* [in Russian], Nauka, Moscow (1964), pp. 5-21.
4. N. S. Gorbachev and G. A. Kashirtseva, "Fluid-melt interaction and evolution of oceanic basalts," in: *Synopses of Physical-Chemical Petrology*, No. 13 [in Russian], Nauka, Moscow (1985), pp. 106-110.
5. E. N. Gramenitskii, "Toward knowledge of the evolution of hydrothermal-magmatic systems," *Vestn. Mosk. Gos. Univ.*, Ser. 4, Geol., No. 2, 3-16 (1986).
6. L. V. Dmitriev, A. Ya. Sharas'kin, G. S. Kharin, and N. A. Kurentsova, "Petrographic characteristics of crustal rocks from the mid-Atlantic ridge rift zone," in: *Investigations into Rift Zone Problems of the World Ocean* [in Russian], Nauka, Moscow (1974), pp. 85-110.
7. I. N. El'nikov, V. M. Litvin, V. G. Gainanov, and V. A. Struchkova, "Acoustical basement relief and sedimentary cover thickness in the region of connection of the Kolbeinsey ridge with the Icelandic rift zone," *Okeanologiya*, 14, No. 5, 782-788 (1984).
8. I. N. El'nikov and G. N. Lunarskii, "Seismic investigations in regions of the Romanche and Guinea gulf depressions, in the first trip of the NIS Akademik Kurchatov," *Okeanologiya*, 10, No. 5, 828-836 (1970).
9. I. N. El'nikov and G. N. Lunarskii, *Sedimentogenesis in the Atlantic Ocean Basin* [in Russian], Nauka, Moscow (1982).
10. E. M. Emel'yanov and G. S. Kharin, "The role of volcanism in the formation of the mineral composition of Recent and late Quaternary sediments of the North Atlantic," in: *Geology of the Atlantic Ocean Floor. Biostratigraphy and Tectonics* [in Russian], Nauka, Moscow (1982), pp. 66-116.
11. D. R. Cann, "Variations in the content of major chemical elements in basalts from the ocean," in: *Petrology of Extrusive and Metamorphic Rocks of the Ocean Floor* [Russian translation], Mir, Moscow (1973), pp. 91-102.

12. G. L. Kashintsev, "Intrusive rocks," in: *Oceanology. Geology of the Ocean. Sediment Accumulation and Magmatism* [in Russian], Nauka, Moscow (1979), pp. 38-68.
13. A. G. Kossovskaya, I. M. Simanovich, and V. D. Shutov, "Mineral transformations of rocks of the oceanic crust, and problems of its initial continentalization," in: *Mineral Transformation of Rocks of the Oceanic Substrate* [in Russian], Nauka, Moscow (1981), pp. 5-16.
14. M. I. Kuz'min and L. P. Zonenshain, "A near-surface magmatic source," in: *Underwater Geological Investigations with Manned Equipment* [in Russian], Nauka, Moscow (1985), pp. 171-174.
15. E. B. Levedev and N. K. Khitarov, *Physical Properties of Magmatic Melts* [in Russian], Nauka, Moscow (1979).
16. M. A. Levitan and A. P. Lisitsyn, "On changes in the intensity of effusive volcanism of the ocean floors in the late Mesozoic-Cenozoic," *Vulcanologiya i Seismologiya*, No. 1, 32-38 (1980).
17. F. A. Letnikov, N. A. Logachev, E. M. Emel'yanov, et al., "The fluid regime of rift zones," in: *Fundamental Problems of Rift Genesis* [in Russian], Nauka, Novosibirsk (1971), pp. 51-60.
18. A. P. Lisitsyn, *Processes of Oceanic Sedimentation* [in Russian], Nauka, Moscow (1978).
19. A. P. Lisitsyn, "The contribution of endogenic material to oceanic sedimentation," in: *Lithology in a New Stage of Geological Development* [in Russian], Nauka, Moscow (1981), pp. 20-44.
20. A. P. Lisitsyn, "Oceanic sedimentary bodies," in: *Geology of the Floor from Deep Water Drilling Data* [in Russian], Nauka, Moscow (1984), pp. 12-61.
21. A. A. Marakushev, "Some questions on petrogenesis in the light of the theory of fluid-magmatic interactions," in: *Problems of the Petrology of the Earth's Crust and Upper Mantle* [in Russian], Nauka, Novosibirsk (1978), pp. 65-83.
22. Yu. P. Neprochnov, A. V. Neprochnova, G. A. Semenov, and N. A. Shishkina, "Structure of the earth's crust and upper mantle from data of deep seismic probing," in: *Oceanology. Geophysics of the Ocean Floor*, Vol. 1 [in Russian], Nauka, Moscow (1979), pp. 243-291.
23. P. P. Timofeev, "Soviet lithology and the path of its development," in: *Lithology in a New Stage in the Development of Geological Knowledge* [in Russian], Nauka, Moscow (1981), pp. 6-19.
24. P. P. Timofeev and V. V. Ereemeev, "Results of lithologic-facies investigations of deposits from deepwater wells," *Tr. GIN*, No. 374, 3-33 (1982).
25. T. I. Frolova, É. N. Zharikov, B. P. Zolotarev, et al., "Magmatic rocks of the floor of the southeastern part of the Pacific Ocean and their secondary transformation in light of the origin of metal-bearing sediments," in: *Metal-Bearing Sediments of the Southeastern Part of the Pacific Ocean* [in Russian], Nauka, Moscow (1979), pp. 48-71.
26. G. S. Kharin, "On the role of halmyrolysis and hydrothermal leaching in supply of ore material to the ocean," *Geokhimiya*, No. 8, 1040-1055 (1978).
27. G. S. Kharin, "The role of volcanic uplifts in avalanche sedimentation and the formation of sediment-rock basins in the ocean (an example from the Iceland region)," in: *Geology of the Seas and Oceans*, Vol. 3 (Theses of the 5th All-Union School of Marine Geology) [in Russian], IOAN SSSR, Moscow (1982), p. 54.
28. G. S. Kharin, "On the connection of several ore components with alteration of basalts," in: *Mineral Transformation of Oceanic Crustal Rocks* [in Russian], Nauka, Moscow (1984), pp. 48-53.
29. G. S. Kharin and Yu. A. Bogdanov, "Basalts of the Romanche deepwater basin," *Oceanology*, 14, No. 4, 677-681 (1974).
30. I. V. Khvorova, "Volcaniclastic accumulations in oceanic sediment cover," *Litol Polezn. Iskop.*, No. 1, 3-26 (1980).
31. F. Aumento, W. G. Melson, et al., *Initial Reports of DSDP*, Vol. 37, US Government Printing Office, Washington (1977), p. 1008.
32. J. L. Bischoff and W. E. Seyfried, "Seawater as a geothermal fluid, chemical behavior from 25 to 350°C," *Proc. 2nd Int. Symp. Water-Rock Interact.*, Strasbourg, 1977, Sec. 4, Strasbourg (1977), pp. 165-172.
33. L. V. Dmitriev, "Petrochemistry of basalts and plutonic rocks," *Initial Reports of DSDP*, Vol. 37, US Government Printing Office, Washington (1977), pp. 681-694.
34. B. Gunn and M. J. Roobol, "Geochemistry of the igneous rocks," *Initial Reports of DSDP*, Vol. 37, US Government Printing Office, Washington (1977), pp. 735-756.

35. R. K. Harrison, R. W. O'B. Knox, and A. C. Morton, "Petrography and mineralogy of volcanogenic sediments from DSDP, southwest Rockall plateau, sites 403 and 404," Initial Reports of DSDP, Vol. 48, US Government Printing Office, Washington (1979), pp. 771-786.
36. J. Honnorez and P. Kirst, "Submarine basaltic volcanism, morphometric parameters for discriminating hyaloclastites from hyalotuffs," Bull. Volcanol., 1975, 39, No. 3, 441-465 (1976).
37. M. Jacque and J. Thouvenin, "Lower Tertiary tuffs and volcanic activity in the North Sea," Petroleum and the Continental Shelf of Northwest Europe, I, Halstead Press (1975), pp. 455-466.
38. J. P. Kennett and R. G. Thunell, "Global increase in Quaternary explosive volcanism," Science, 187, No. 4176, 497-501 (1975).
39. W. G. Melson, T. I. Vallier, T. L. Wright, et al., "Chemical diversity of abyssal volcanic glass erupted along Pacific, Atlantic, and Indian Ocean sea-floor spreading centers," in: Geophysics of the Pacific Ocean Basin and Margin, Washington, DC (1976), pp. 351-367.
40. J. S. McLain, J. A. Orcutt, and M. Burnett, "The East Pacific rise in cross section: a seismic model," J. Geophys. Res., B, 90, No. 10, 8627-8639 (1985).
41. M. J. Mottl, H. D. Holland, and R. F. Corr, "Chemical exchange during hydrothermal alteration of basalt by seawater. II. Experimental results from Fe, Mn, and sulfur species," Geochim. Cosmochim. Acta, 43, No. 6, 869-884 (1979).
42. G. K. Muecke, J. M. Ade-Hall, F. Aumento, et al., "Deep drilling in an active geothermal area in the Azores," Nature, 252, No. 5481, 281-285 (1974).
43. K. N. Wedepohl, "Tholeiitic basalts from spreading ocean ridges: the growth of the oceanic crust," Naturwissenschaften, 68, No. 3, 110-119 (1981).

SECONDARY MINERALS OF THE SLOPE DEPOSITS ON THE
MAGELLAN SEAMOUNTS (PACIFIC OCEAN)

S. G. Skolotnev, G. V. Karpova,
and E. V. Pokrovskaya

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In the article, we discuss the material composition of the following indigenous rocks: basalts and tuffs constituting the volcanic basement of the Ita Mai Tai and IOAN guyots among the Magellan Seamounts and also slope formations represented by clastic rocks: breccias, sandstones, silty clays, and turbidites. We show that products of the hydrothermal conversions of basalts and tuffs play an important role in the composition of the clastic rocks.

The indigenous rocks of the ocean floor, represented primarily by basalts, are one of the distributive provinces associated with oceanic sedimentation. It has been established that the conversion products of basalts are the most important contribution to pelagic sediment formation [1, 2, 3]. Their role in the formation of sedimentary strata are especially important in a region of large-scale positive oceanic morphostructures, such as describes the Magellan Seamounts located in the East Mariana Basin, in particular. The Magellan Seamounts have a volcanic origin and were apparently formed in early Cretaceous times on oceanic crust of Jurassic age.

During the 9th voyage of the scientific-research vessel Academician Mstislav Keldysh, the guyots of Ita Mai Tai (coordinates 156°25'-157°15' E and 13°13'-12°37' S) and IOAN (coordinates 155°44'-156°41' E and 14°26'-13°43' S) were studied in detail.

The top of the Ita Mai Tai guyot is located at a depth of 1400-1478 m. As a result of dredging the gentle areas on the western slope of the guyots at depths of 2580-2700 m (station 1038) and 4000-4150 m (station 1053) (Fig. 1a), we discovered basaltoids characterizing the volcanic basement. Stony material was obtained in the form of individual fragments with dimensions of 5-15 cm (sample 1038/1-5) and one large block 1.5 m in the perpendicular (sample 1053) covered from one side by a crust of ferromanganesian oxides up to 0.5 cm in thickness. Several fragments of dense silty brownish-red and rose colored clays of 5-30 cm dimensions were uncovered besides the basaltoids. The clay fragments were impregnated with lines of muds (sample 1053/1-10). The fragments of clayey rock had rounded shapes and were covered with ferromanganesian oxides of various thicknesses, ranging from thin prisms to thicknesses of up to 1 cm. Consequently, they slid down from above at various times when the areas of their original deposition were disturbed.

At the volcanic base of the Ita Mai Tai guyot, the deposits are predominately limestones discovered by three boreholes (200-202) drilled from the ship Glomar Challenger. The drilling penetrated more than 100 m to oolitic limestones, probably of Aptian age, without reaching the volcanic base.

The top of the IOAN guyot is located at depths of 1482-1479 m. Samples of the rocks characterizing the volcanic basement of the guyot were obtained from depths of 2020-1550 m during dives of the POA "Pisces" and also during trawling carried out on a gentle area of the slope at a depth of 3800-4200 m. As a result of seven dives, we were able to characterize the western slope of the guyot (stations 1056-1059, 1063) and the southwestern slope of its eastern satellite (stations 1069-1070) (see Fig. 1b). Volcanic material was discovered in the form of individual large (up to 70 cm) and small (5-10 cm) lumps of basalts primarily from massive lava flows (samples 1056/5, 6; 1059/1, 7, 8, 9; 1063/1, 5, 6, 7) and, more rarely, pillow lavas (sample 1058/1, 4, 7) and brecciated lavas (samples 1063/2 and 1069/1). Basalts uncovered in significant quantities were present in the form of breccias (samples 1058/2; 1059/5; 1063/3, 4; 1069/6, 7, 8, 11; 1070/5). Besides the basalts, volcanic material was

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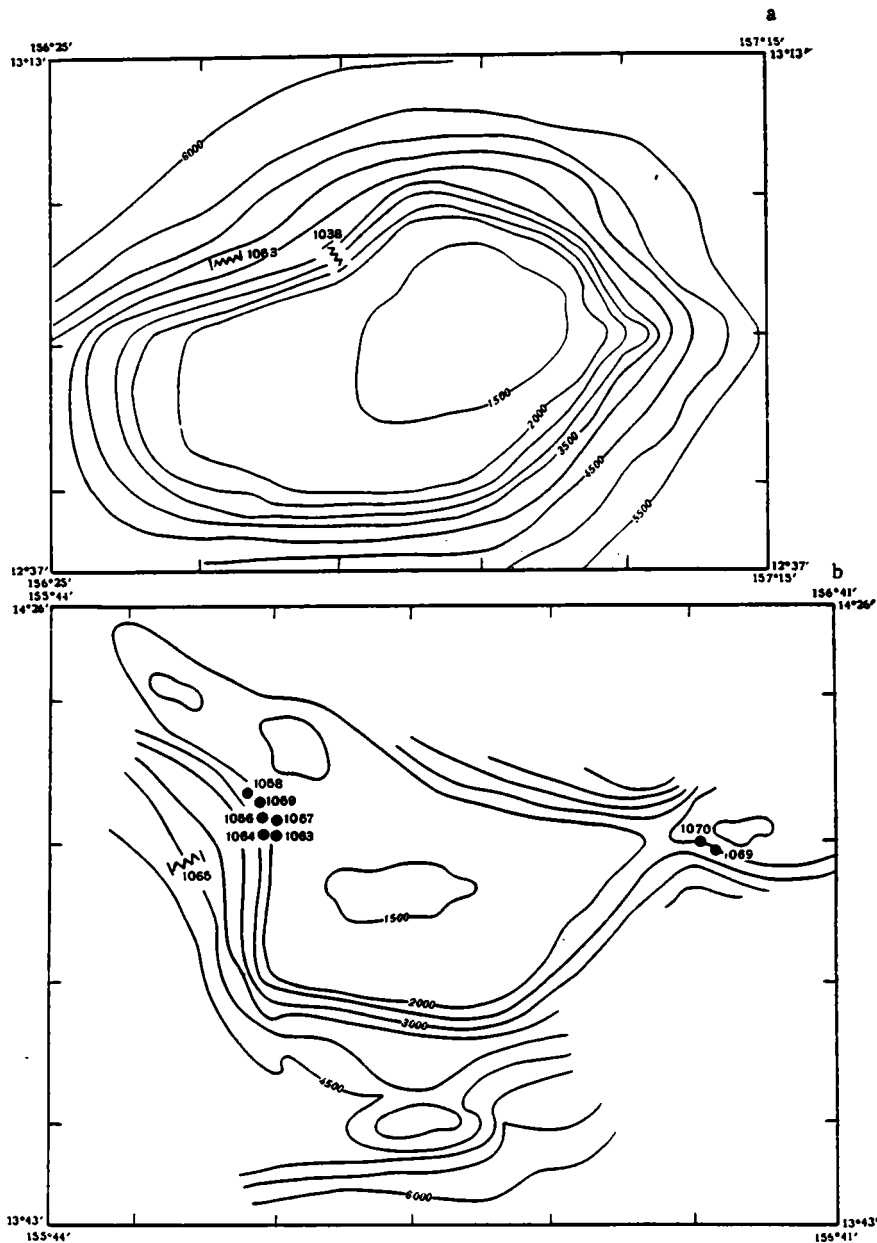


Fig. 1. Bathymetric sketch-map of the Ita Mai Tai (a) and IOAN (b) guyots. The station of the POA "Pisces" and its number are noted; the wavy line corresponds to the trawling station.

represented by tuffs in the form of fragments of comparatively small (3-10 cm) dimensions (samples 1056/3; 1058/3, 6, 10; 1070/6, 7). At station 1069, fragments of sandstone were discovered in addition to volcanic material (samples 1069/2, 3). All of the individual fragments and breccias were covered or partially covered on all sides by a thick (5-15 cm) ferromanganese crust.

On the basis of a petrographic study of the material discovered and NSP data (seismic data obtained by I. H. El'nikov), it can be concluded that the upper portion of the volcanic section of the IOAN guyot is an interlayering of basaltic and tuffaceous horizons. Limestones occur upwards along the section. Sandstones lie on the terracelike areas on the top portions of the slope.

Dredging of the slope was conducted at station 1065. Several lumps of basalts with dimensions of up to 50 cm were discovered (samples 1065/5, 6). Clastic rocks of various dimen-

sions were discovered in significant quantity during the dredging. These rocks were represented by several light-green lumps (10-30 cm) (samples 1065/1-4) and by pebbly material (sample 1065/10). The lumps were predominately composed of fragments of altered tuffs. Several of the tuffs had the layered, rhythmical structure characteristic of turbidites. The clastic rocks were completely devoid of a ferromanganesian-oxide cover and were very weakly cemented; this allows us to suppose that they were formed recently as a result of a disturbance of overlying tuff deposits and transfer of material downward in the form of turbid flows.

The pebbly material consists of rounded pebbles of 1-4-cm dimensions primarily represented by basalts (80%) and, more rarely, tuffs (20%).

Thus, basalts, tuffs, sandstones, turbidites, silty clays, and breccias play a role in the samples of the volcanic basement of the guyots and the slope deposits. The material compositions of these rocks are discussed below.

Basalts. Petrography and Chemical Composition. On the basis of high values for TiO_2 and total alkales and relatively low values for $\text{Na}_2\text{O}/\text{K}_2\text{O}$, the basalts discovered can be assigned to a series of subalkaline basalts. Four groups are distinguished among them, forming a differentiated series ranging from subalkaline basalts to hawaiites. The basalts of the first group were discovered at station 1069. These are practically aphyric low-porosity rocks with a significant quantity of olivine subphenocrysts (10%). The ground mass is characterized by widely occurring labradorite and ore minerals (up to 15%). Relatively low silica content and very high iron content are characteristic of these rocks (Table 1, sample 1069/7). Basalts of the second group were found at stations 1058 and 1065. These are also aphyric rocks, but they are intensely and coarsely porous and contain small (2-5%) quantities of olivine microphenocrysts. The ground mass consists of plagioclase microlites of andesitic composition and skeletal, needle-shaped microlites of olivine. They can be distinguished chemically by higher contents of silica and alkalies, and significantly lower iron content and $\text{Na}_2\text{O}/\text{K}_2\text{O}$ ratio (see Table 1, samples 1058/2a; 1058/4, 7; and 1065/6). The third groups basalts (stations 1038, 1053, 1056, 1057, 1059, and 1070) were the most represented. Microlites of plagioclase similar to andesite and less abundant titanaugites and titanomagnetites play a role in the composition of the groundmass. In several varieties, olivine microlites are abundant in place of titanaugite. These are intensely porous basalts. Chemically, they are characterized by a still higher alkali content and a still lower $\text{Na}_2\text{O}/\text{K}_2\text{O}$ ratio (see Table 1, samples 1038/1; 1053/12; 1056/5, 6; 1059/8). The basalts of the fourth group were discovered at station 1063 and are characterized by the highest alkali content and the lowest $\text{Na}_2\text{O}/\text{K}_2\text{O}$ ratio (see Table 1, samples 1063/2a, 6, 7). These are rare olivine-porphyrific rocks with a trachytoidal ground mass consisting of approximately equal quantities of olivine and andesite microlites and a relatively small quantity of powdery segregations composed of ore minerals.

The basalts, characterized by high (10-30%) porosity, have two types of pores distinct in dimensions and morphology. The coarse pores with dimensions ranging from 0.5 to 8 mm are usually are nearly circular in shape. Small pores (0.05-0.25 mm) have either ameboid or angular shapes and are characterized by interstitial positions in the groundmass. The borders of the microlites frequently protrude into them.

The high porosity of the basalts and the presence of tuffaceous interlayers suggest shallow-water outflows of basaltic lavas and even subaerial outflows in cases when high-temperature oxidation of the basalts can be detected.

Secondary Minerals. The secondary minerals in all of the groups of basalts are untypical, with some exceptions. Nontronite, lesser amounts of goethite, and a mineral similar to glauconite are the most abundant minerals in the crystalline varieties. Glauconite is a bright-green clay mineral usually possessing high contrast and superimposed light-green interference colors. Nontronite is a pale green mineral with a refractive index significantly lower than that for glauconite; it possesses bright-silver to yellow interference colors. The diagnostic clay minerals are presented below.

The transformation of the vitreous varieties of the basalts is expressed in the palagonitization of the sideromelane glass and in the subsequent development of smectite inheriting the composition of the palagonite and ferric hydrates (samples 1058/7; 1063/2). The details of these secondary products will be discussed below when describing the material composition of the tuffs.

TABLE 1. Chemical Compositions of Rocks Raised up from the Slopes of Submarine Mountains

Com- ponent	Basalts										Tuffs						Silty clays		Sandstones		Turbidites	
	1069/7	1058/2A	1058/4	1058/7	1065/6	1038/1	1053/12	1056/5	1056/6	1059/8	1063/2A	1063/6	1063/7	1070/6	1058/6	1058/3	1053/1	1053/8	1069/3	1069/2	1065/1	1065/3
SiO ₂	39,63	39,35	36,77	40,99	47,25	49,83	47,51	43,64	42,62	42,78	34,49	47,85	46,72	36,48	43,68	42,29	50,25	47,24	30,82	33,86	42,89	45,17
TiO ₂	2,12	2,79	1,27	2,60	2,33	1,83	2,20	1,72	1,74	1,57	2,61	2,38	2,40	1,02	2,12	1,78	1,92	2,27	1,86	1,89	2,76	2,13
Al ₂ O ₃	18,09	16,82	12,24	16,61	15,20	17,13	17,80	15,08	14,68	15,37	19,56	15,55	14,71	12,15	14,23	13,08	13,14	14,93	9,32	10,74	13,26	14,33
Fe ₂ O ₃	13,68	17,65	11,00	15,65	10,84	9,39	9,96	8,04	8,62	8,62	14,08	8,89	7,45	11,88	12,94	11,93	10,08	9,83	10,00	12,77	11,99	12,20
FeO	2,43	0,79	—	0,29	0,39	1,18	1,97	0,51	0,55	0,35	0,37	0,26	0,25	0,15	0,43	—	0,31	0,45	1,42	0,57	0,29	0,36
MnO	0,23	0,21	0,31	0,02	—	0,10	0,12	0,19	0,14	0,01	0,03	0,04	0,07	0,03	0,03	0,34	0,17	0,20	0,21	0,22	0,04	0,16
CaO	8,79	1,72	15,22	0,85	7,47	6,61	7,80	10,45	10,27	11,02	4,85	6,57	8,85	8,57	2,19	3,17	1,30	2,01	14,89	12,74	2,64	1,04
MgO	2,72	2,20	1,79	2,30	1,90	1,58	1,54	2,82	2,55	1,54	1,85	2,36	2,20	4,82	3,12	3,29	3,56	3,45	3,54	2,79	3,26	3,42
Na ₂ O	2,70	1,01	2,70	1,75	3,61	4,28	4,37	3,84	3,84	3,18	3,65	3,98	3,80	2,94	1,89	1,78	2,55	3,25	1,67	1,82	2,94	2,43
K ₂ O	0,84	1,53	1,85	2,44	1,84	2,93	2,28	2,60	2,77	2,77	1,52	3,41	3,80	3,93	2,93	2,77	4,75	3,61	1,82	1,82	1,85	2,34
H ₂ O ⁻	0,38	7,93	2,91	9,10	4,23	1,78	1,41	3,10	3,03	3,02	5,12	2,92	2,51	7,02	9,50	Not det.	6,53	6,32	6,57	5,51	11,58	10,39
H ₂ O ⁺	5,98	7,46	2,92	7,02	2,90	2,08	1,83	2,15	2,19	2,83	5,81	2,07	1,64	5,42	5,70	—	4,20	5,59	4,93	4,94	5,28	5,59
CO ₂	—	—	0,60	—	0,30	—	—	0,70	—	—	—	—	—	0,50	—	—	—	—	0,80	0,45	0,90	—
P ₂ O ₅	1,96	0,47	10,36	—	0,96	0,86	0,73	4,68	6,80	7,90	0,68	3,17	6,05	5,12	0,81	1,82	1,76	0,33	12,16	8,33	0,07	—
Σ	99,55	99,93	99,94	99,62	99,21	99,57	99,52	99,52	99,80	100,96	99,62	99,45	100,45	100,02	99,57	82,28	100,52	99,48	99,99	98,62	99,75	99,56

*Note. The analyses were performed in the chemical laboratory of the Institute of Geological Sciences, Academy of Sciences of the USSR

TABLE 2. Chemical Composition of Secondary Minerals

Com- ponents	I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII
SiO ₂	48,86	51,04	50,01	5,49	48,51	47,54	39,48	41,31	52,78	51,40	43,51	40,66	43,90
TiO ₂	0,12	0	0	0,70	0,07	0,02	0,19	0,09	0,16	0,68	1,74	1,34	0,02
Al ₂ O ₃	3,53	1,29	4,37	1,92	3,69	5,78	7,74	3,26	5,46	13,84	16,25	15,74	16,24
FeO	36,79	25,53	25,75	64,52	30,33	31,22	30,99	34,46	23,19	14,70	13,32	17,05	15,33
MgO	4,35	5,10	4,73	1,97	3,37	2,91	8,64	2,92	4,81	4,22	4,07	3,92	13,80
CaO	0,32	0,15	0,10	0,23	0,14	0,14	0,27	0,03	0,44	0,24	0,11	0,15	0
Na ₂ O	0,64	0,09	0	0,28	0,16	0,20	1,08	0,62	0,88	0,47	0,62	0,73	0,84
K ₂ O	4,11	7,85	7,96	0,09	6,50	5,78	2,69	5,43	4,29	4,04	4,13	4,15	1,27
MnO	0	0,09	0	0,07	0	0,04	0,14	0,03	0,01	0,01	0	0,03	0,08
P ₂ O ₅	0	0	0	0	0	0	0,06	0,09	0	0	0,12	0,09	0
Σ	96,72	90,86	92,02	75,27	92,76	93,62	91,27	88,23	92,04	89,59	83,86	83,36	91,49

Explanation. I-IV: Sample 1053/12. I) brown mineral infilling the inner portion of the vein, II) bright-green mineral composing the selvage of the same vein, III) bright-green mineral partially replacing olivine phenocryst, IV) iddingsite, replacing the same olivine phenocryst. V-VIII: sample 1056/6. V) bright-green mineral infilling nucleus of a concentrically zonal vesicle; VI) same, composing peripheral zone, VII) red-brown mineral infilling nucleus of the previously mentioned vesicle; VIII) brown material composing peripheral zone of concentrically zonal vesicle. IX: sample 1059/7 (a pale-green material completely infilling an amygdale). X: sample 1058/6 (smectite replacing vitreous fragment of tuff). XI-XIII: sample 1070/6; XI) smectite composing incrustate ring; XII) smectite infilling vitreous fragment of tuff; XIII) smectite forming circular feature within the glass.

The analyses were performed on a "Kamebaks" microanalyzer.

Minerals which are varieties of apatite also widely occur in the brecciated basalts.

The secondary minerals in the crystalline varieties of the basalts either completely or partially occupy veins, vesicles, and pores and also either partially or completely replace grains of olivine and plagioclase. The filling of the vesicles and pores with clay minerals takes place in zones; glauconite reached a limited distribution. It usually concentrates in a zone of 0.5-2 cm thickness, either bordering one of the edges of the sample or distributing itself along several cracks (samples 1056/5, 6; 1058/1, 2, 4, 7; 1059/6, 6, 8; 1063/1, 1069/11, 1070/8a). In this zone, glauconite forms coagulation crusts with thicknesses of 0.05-0.1 mm in large vesicles and completely fills the small pores located interstitially.

The relatively large vesicles in this zone frequently have a concentrically zonal structure. In such cases, the peripheral layer is composed of glauconite and the inner layer is composed of nontronite and has either the same thickness or completely occupies the remaining space. Sometimes, apatite is deposited after the nontronite. The glauconite often takes of a brownish tint as a consequence of an admixture of ferric hydrates.

In the majority of samples, nontronite is predominately found in the remaining volume outside the zone of glauconite occurrence in the vesicles and pores. In individual samples, nontronite forms a thin coagulation crust of 0.01-0.2 mm thickness on the walls of the pores; in other samples, it completely fills the pores and partially or even completely replaces plagioclase microlites (samples 1056/5, 6; 1063/6; 1069/6). There are also common cases of concentrically zonal infilling of pores in this area of rocks. In such cases, the peripheral layer is composed of nontronite and the inner layer is composed mostly of apatite, but sometimes calcite (sample 1063/1), zeolite (samples 1065/6; 1069/1), or calcite and zeolite with an earlier segregation of the first (sample 1065/7).

Sample 1058/7, possessing a vitreous texture in its groundmass, is characterized by a rhythmical zonality and a distribution of secondary minerals throughout the volume of the rock. Pores in a zone of 0.3 cm thickness at the very top of the sample are partially or completely infilled with glauconite. Lower, in a zone of 0.4 cm thickness, the pores are empty. Still lower is a zone of 0.25 cm thickness in which the infilling of the pores is concentrically zonal in character; in the center, there is a red iddingsitelike material. Finally, there is a zone of 0.3 cm thickness in which a concentrically zonal infilling of the pores also occurs: the periphery is glauconite; the center is nontronite. A fine incrustation of nontronite can be seen in the pores over the remaining extent of the sample.

We did not detect a zonality in the distribution of clay minerals within all of the samples. In sample 1038/1, all of the pores occupying interstitial positions (3-5%) are completely filled with glauconite. In sample 1053/12, almost all of the vesicles and interstitial separations are filled with a red iddingsitelike material and regions are only spottily present where glauconite is encountered. Glauconite was absent in the following samples: 1059/1, 4, 7; 1063/2, 6, 7; 1065/5, 6; 1069/1, 6, 7, 8. Only nontronite had developed from the plagioclase; but in the pores in sample 1069/8, nontronite only had developed from the interstitial glass.

The phenocrysts and microlites of olivine have undergone a complete conversion; this is reflected in the exceptionally low MgO content in the basalts studied (see Table 1). The olivine microlites universally have a red color as a result of their replacement by goethite. The conversion of the olivine phenocrysts is azonal in the majority of the samples. They are completely replaced by iddingsite throughout the entire volume of the sample (samples 1038/1; 1053/12; 1058/2; 1059/1, 4-7; 1069/1, 7, 8). Nevertheless, the secondary products which have developed from olivine in a number of samples are subject to the above described zonality. In samples 1056/5, 6; 1058/4; 1059/8; 1063/1, 10; and 1070/8, olivine phenocrysts in the zone of glauconite occurrence are iddingsitized; whereas they are replaced by nontronite in the remaining spaces.

Samples 1059/1, 4, 6, and 7 are distinguished by a special peculiarity with respect to secondary minerals. A segregation of finely dispersed hematite in the ground mass is characteristic of these samples and the grains of plagioclase are partially replaced by potassium feldspar. The segregation was formed during high-temperature oxidation of basalts under sub-aerial conditions [5]. As is well known, it is precisely at high oxidation potential that the activity of potassium in sea water reaches values at which plagioclases undergoes K-feldspathization.

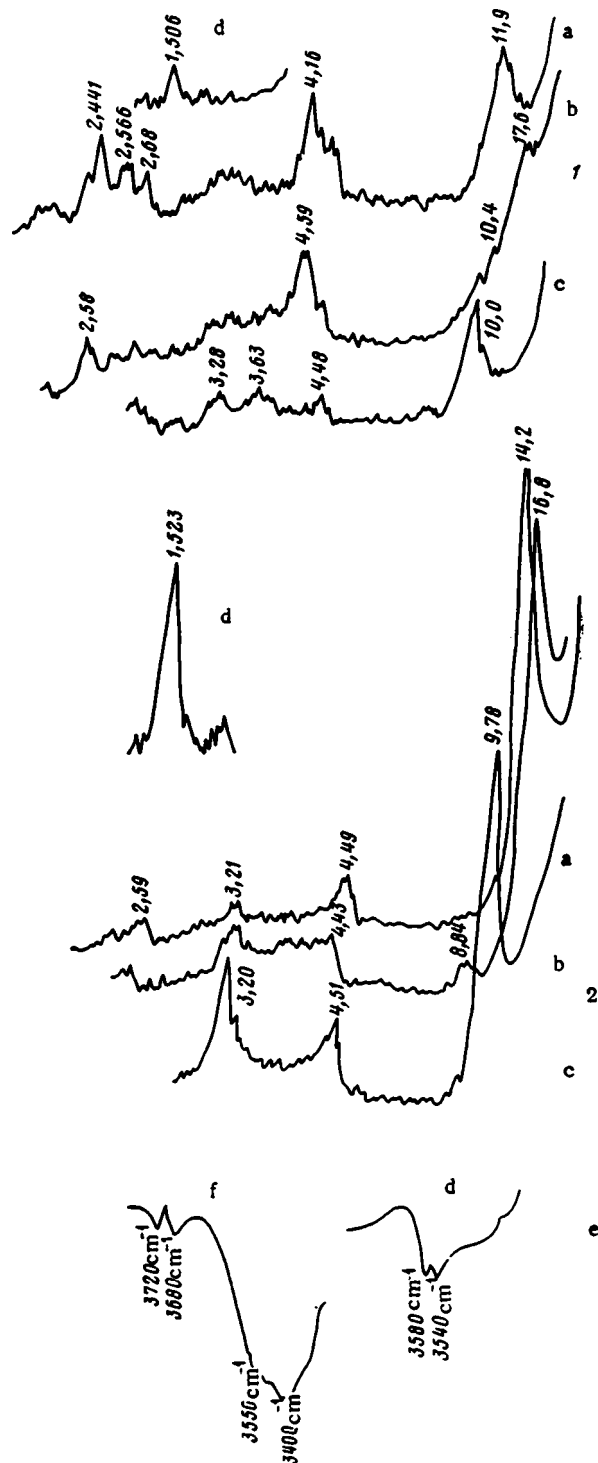


Fig. 2. Diffractograms and IR spectra of secondary minerals in basalts 1) pseudomorphs after olivine (sample 1053/12); 2) smectite infilling the pores and forming pseudomorphs after olivine (sample 1056/6); 3) IR-spectra of sample 1056/6 (a: original sample; b: saturated with ethylene glycol (sample 1053/2), with glycerine (sample 1056/6); c: heated; d: d_{060} ; e) oriented sample; f: pellet of sample with KBr powder).

The veins in the basalts are primarily infilled with apatite; the infilling is represented by clay minerals in rare cases. In particular, in sample 1053/12, zonal veins occur in which the selvage is represented by glauconite, the more inward layer represented by goet-

hite, and the center, infilled with a red-brown material, is represented by a mixture of glauconite and goethite.

The chemical and phase properties of the secondary minerals present in the crystalline basalts were studied in samples 1053/12; 1056/6; and 1059/7. Glauconite and goethite were present in sample 1053/12; only nontronite was present in sample 1059/7, while sample 1056/6 was characterized by a zonal distribution in which glauconite occurred at one edge of the sample but nontronite was abundant in the remaining volume.

For the x-ray phase analysis of the glauconite, we selected pseudomorphs after olivine from sample 1053/12; the pseudomorphs were composed of iddingsite in association with glauconite, with a conversion of the former. X-ray photographs of the original and treated samples (saturated with ethylene glycol and heated) allowed us to find three phases in the selected fraction: goethite, dioctahedral ($d_{060} = 1.506 \text{ \AA}$) smectite (d_{001}) corresponded to 11.9, 17.17, and 10 $\text{\AA}$, respectively) and hydromicas (on the basis of the appearance of a weak reflection, $d_{001} = 10.4 \text{ \AA}$ in the saturated sample) (Fig. 2, 1).

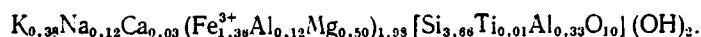
The chemical composition of the glauconite was studied with the aid of a microprobe. We analyzed its segregation in a vein (see Table 2, II), in a pseudomorph after olivine (see Table 2, III), and in vesicles (see Table 2, IV). The results obtained from the analyses were fairly consistent with one another. Their recalculation in the crystallochemical formula for a clay mineral according to the standard methodology for 22 negative charges suggests that the iron mainly occurs in the oxidized form. Taking into account the results of the x-ray photographs, the conversion allows us to identify that these minerals are glauconites containing swelling layers within their structures



The chemical compositions of the brownish-green minerals closely associated with glauconite (see Table 2, I, VIII) are similar to the chemical composition of the latter, but differ in their elevated iron content. The difference can be explained, in this case, by the presence of an admixture of ferric hydrates in the glauconite, a presence confirmed by microscopic observations.

The chemical composition of the iddingsite is markedly dominated by the iron content, along with small additions of SiO_2 , Al_2O_3 , and MgO (see Table 2, IV). Taking into consideration the x-ray data, it is logical to conclude that the iddingsite is represented by a fine mixture of goethite and dioctahedral smectite.

The nontronite for the x-ray phase analysis was isolated from sample 1056/6. The x-ray study showed that this is a dioctahedral smectite (d_{001} equaled 14.2, 16.8, and 9.78 $\text{\AA}$, respectively for the original, saturated, and heated samples) with $d_{060} = 1.523 \text{ \AA}$; this is characteristic of nontronite (see Fig. 2, 2). Nontronite localized in a vesicle in sample 1059/7 was studied with the aid of a microprobe. The chemical composition of this mineral (see Table 2, IX) is essentially indistinguishable from the chemical composition of glauconite. If one compares principal oxide contents, this is less of a potassium and ferruginous mineral, and more of a siliceous one. More significant and perhaps major differences concern the content of minor oxides. This mineral contains several times more TiO_2 , Na_2O , and CaO . Recasting of the analysis into the crystallochemical formula using the standard methodology, with allowances made for the x-ray data, allows us to identify this mineral as a low-charge nontronite:



A red-brown material occurs in small quantities in sample 1056/6, where it infills the nuclei of concentrically zonal vesicles in which the peripheral layer is composed of glauconite. The borders between the vesicles are uneven and, possibly, glauconite is being replaced by this substance. Its chemical composition was also investigated with the aid of a microprobe (see Table 2, VII). It differs significantly from the composition of glauconite and nontronite, first of all, with respect to the elevated content of magnesium and aluminum and the lowered content of K_2O . This material is probably a fine mixture of ferric hydroxides

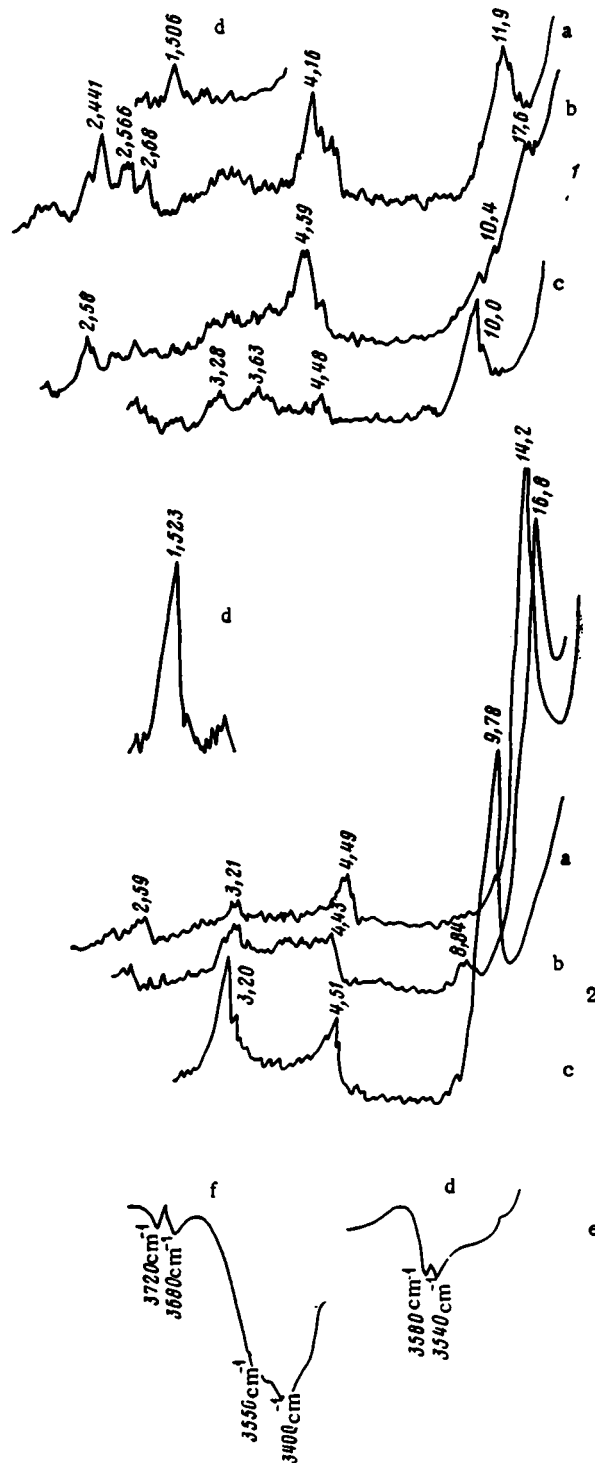


Fig. 2. Diffractograms and IR spectra of secondary minerals in basalts 1) pseudomorphs after olivine (sample 1053/12); 2) smectite infilling the pores and forming pseudomorphs after olivine (sample 1056/6); 3) IR-spectra of sample 1056/6 (a: original sample; b: saturated with ethylene glycol (sample 1053/2), with glycerine (sample 1056/6); c: heated; d: d_{060} ; e) oriented sample; f: pellet of sample with KBr powder).

The veins in the basalts are primarily infilled with apatite; the infilling is represented by clay minerals in rare cases. In particular, in sample 1053/12, zonal veins occur in which the selvage is represented by glauconite, the more inward layer represented by goet-

hite, and the center, infilled with a red-brown material, is represented by a mixture of glauconite and goethite.

The chemical and phase properties of the secondary minerals present in the crystalline basalts were studied in samples 1053/12; 1056/6; and 1059/7. Glauconite and goethite were present in sample 1053/12; only nontronite was present in sample 1059/7, while sample 1056/6 was characterized by a zonal distribution in which glauconite occurred at one edge of the sample but nontronite was abundant in the remaining volume.

For the x-ray phase analysis of the glauconite, we selected pseudomorphs after olivine from sample 1053/12; the pseudomorphs were composed of iddingsite in association with glauconite, with a conversion of the former. X-ray photographs of the original and treated samples (saturated with ethylene glycol and heated) allowed us to find three phases in the selected fraction: goethite, dioctahedral ($d_{060} = 1.506 \text{ \AA}$) smectite (d_{001}) corresponded to 11.9, 17.17, and 10 $\text{\AA}$, respectively) and hydromicas (on the basis of the appearance of a weak reflection, $d_{001} = 10.4 \text{ \AA}$ in the saturated sample) (Fig. 2, 1).

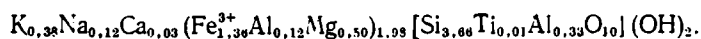
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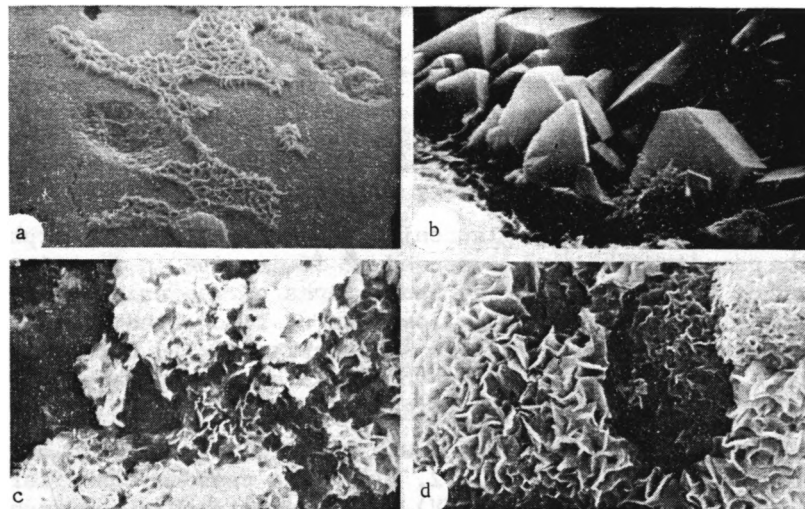


Fig. 3. Photomicrography of smectites and zeolites replacing tuffs (magnification 20,000): a) smectites replacing tuffs (samples 1070/6); b) zeolites (sample 1070/6); c) smectites replacing ash deposits (sample 1053/2); d) smectites developing from tuff fragments composing turbidites (sample 1065/3).

and ferruginous saponite. The presence of the trioctahedral phase among the clay minerals of sample 1056/6 is confirmed by the data from IR spectroscopy (Fig. 2, Part 3). If it is true that the absorption bands of the $\text{Fe}_2^{3+}\text{OH}^-$ (3540 cm^{-1}) and that $\text{Fe}^{2+}\text{OH}^-\text{Al}$ (3580 cm^{-1}) bonds characteristic of dioctahedral minerals can be identified on the IR spectrum of an oriented sample in the region of the valent oscillations of the OH^- group, then it is also true that the two small absorption bands at 3680 and 3720 cm^{-1} characteristic of Mg_3OH^- bonds in trioctahedral minerals containing potassium within their interlayers can be detected (in addition to the above-mentioned bands) in an unoriented sample photographed using KBr.

The apatite is localized in pores and veins, having segregated there after the clay minerals; it partially or completely replaces grains of plagioclase (samples 1056/5, 6; 1058/1, 2, 4; 1059/5, 7; 1063/2, 6, 7; 1069/1, 6), and replaces olivine phenocrysts in rare cases. It forms aggregates of very fine, isometric, translucent grains. Such aggregates are widely occurring in the cement of the tuffs. We removed this type of aggregate from tuffs and identified them by the x-ray phase method. One of the apatite varieties was identified, according to a set of reflections on diffractograms, as either francolite or dernite. A final identification would only be possible with a determination of the chemical composition of the mineral. These are low-temperature carbonate-hydroxyapatites found in sedimentary rocks.

The widespread occurrence of apatite in these basalts is strongly reflected in the chemical composition of the altered rocks (see Table 1, sample 1069/7; 1058/4; 1056/5, 6; 1059/8; 1063/6, 7). High values of CaO correlate with high P_2O_5 content. The overall effect of the processes of secondary transformation upon the chemical composition of the crystalline basalts is expressed in the decrease in the magnesium content and the increase in the content of potassium, water, and, in individual cases, calcium and phosphorous; it is also expressed in the almost complete oxidation of iron. A decrease in the content of CaO , Na_2O , and Al_2O_3 is characteristic of the vitrobasalts (see Table 1, samples 1058/2a, 1058/7, and 1063/2a).

Stage of Basalt Conversion. Thus, we have found specific paragenetic association of secondary minerals in the subalkalic basalts of the Ita Mai Tai and IOAN guyots. The earliest conversions were glauconite containing swelling layers within its structure and, apparently, iddingsite. The glauconite is often associated with goethite. The next phases within time of the conversion are nontronite (also often associated with goethite) ferruginous saponite, and potassium feldspar. Finally, apatite is last in order of conversion, except in samples discovered at great depths, where calcite and phillipsite have that distinction.

The clay minerals described above are fairly widely distributed within oceanic basalts, in particular, within the submarine basalts which compose submarine mountains. V. B. Kurnosov [4] and others associate the formation of these clay minerals with the interaction of basalts with hydrothermal solutions. According to Kurnosov, the magmatic chamber causes

(while not completely extinguished) circulation of sea water through penetrable basalt strata by means of convective cells encompassing the entire volcanic edifice. The sea water is heated while moving from the periphery to the pipe of the volcano; it acquires acidic properties in the process and is mineralized by the leaching of material from the basalts and tuffs. Because of the character of the rock material collected, we studied only the basalts of the peripheral areas of the volcanic edifice. Oxidative conditions of mineralization are characteristic of these areas, since a high oxidative potential is natural to areas weakly metamorphosed by sea water. Under these conditions, iron, easily leached from the basalts, possesses a slight mobility. This leads to a widespread distribution of ferric hydroxides and ferruginous clay minerals. Potassium possesses elevated activity under oxidative conditions and relatively low temperature; this is apparently due to the K-feldspathization of plagioclases. To a substantial degree, the source of the potassium is apparently sea water.

The two stages of clay formation observed allow us to propose that the earliest of them (glauconite and iddingsite) occupying a narrow zonal position in the rock, were possibly still being formed during the interaction of the sea water with hot lava flow at the moment of its outpouring. The sea water in the hot lava flow would have penetrated into the contraction fissures in this case.

Apatite occurs not only in the volcanogenic rocks but also replaces the carbonate cement in breccias and the organic limestones either raised up from the slopes of the submarine mountains or composing the sections overlying the volcanic basement of the guyots. Apatite is differently distributed in different fragments of basalts. It is absent in those fragments which recently detached from the slope. These observations provide a basis for suggesting that the apatite in the basalts is unassociated with hydrothermal solutions and has a halmyr-olytic nature. The question of the origin of the phosphate remains open.

Tuffs. These are soft rocks with a light green color as a consequence of their complete replacement by secondary products. They are encountered predominately in the form of separate fragments (up to 10 cm) which are nuclei of ferromanganesian concretions (1056/3, 1058/10) or relatively large (up to 25 cm) lumps (1070/6, 7). More rarely, tuffs occur within the compositions of breccias, together with basalts or limestones (1056/4), (1057/4). Samples 1058/3, 6 were collected from a basement slope. Lapillic (1070/6, 7), psephitic (1058/3, 6; 1056/3), and psammitic (1058/10, 1057/4) varieties can be distinguished on the basis of grain size. The coarse-grained varieties are predominately composed of isometric, completely rounded fragments possessing odd border contouring as a consequence of the high porosity of the constituent rocks. A total absence of sorting is characteristic of these varieties. The dimensions of the fragments vary from 3 mm to 2 cm in the lapillic tuffs and vary from 1 to 7 mm in the psephitic-psammitic tuffs. The psammitic tuffs are composed of tabular, angular, and horn-shaped particles generally forming a gradational layering in a rhythm of up to 5-mm thickness. The sizes of the particles in the psammitic tuffs apparently decrease in the upward direction from 1.5 to 0.2 mm.

The petrographic compositions of the fragments of all the identified varieties are identical and surprisingly homogeneous. They are all composed of intensely vesicular (porosities amounting to 30-50%, pore dimensions of 0.02-1 mm) vitreous fragments apparently having earlier possessed a basaltic composition. Some of the fragments contain approximately 5-10% plagioclase microlites (samples 1070/6, 7) or iddingsitized olivine (samples 1058/3, 6). These are thus vitroclastic basalts.

The glass is completely replaced by a pale-green, finely dispersed clay mineral forming a concentric zonality around pores (in a zone of up to 0.5 mm) which appear in an alternation of thin bands possessing different shades of reddish-brown and green and showing various manners of birefringence. Between concentrically zonal areas, the glass is sometimes replaced by a reddish-brown, practically isotropic palagonite of coarse texture. All of the edges of the fragments are outlined with an incrustate rim of an analogous pale-green smectite which is highly birefringent and which also possesses a concentrically zonal structure. The thickness of the rim is 0.02-0.05 mm. Such rims occur on the walls of the pores. Rosettes of phillipsite with diameters of up to 1 mm often grow on the incrustate rims, both within the pores and in the between-fragment spaces.

The microlites and phenocrysts of olivine existing in the glass are iddingsitized and the microlites of plagioclase are K-feldspathized. The cementation of the fragments is uneven: ranging from a pellicular type to a type with infilling of the pores. The cement is an incrustation of clay mineral, zeolite, and the carbonate-phosphate material described above.

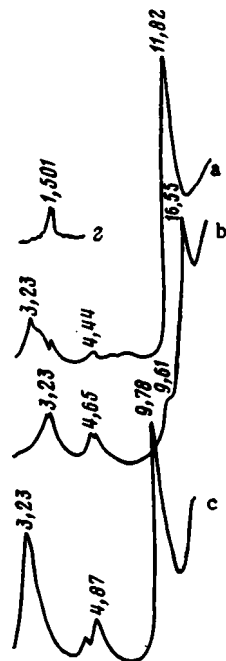


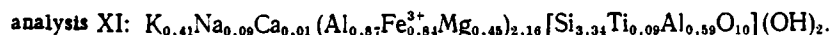
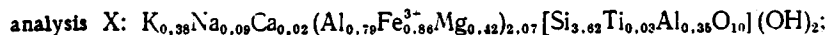
Fig. 4. Diffractogram of smectite replacing tuff (sample 1056/3) a) original sample; b) saturated with ethylene glycol; c) heated; d) d_{060} .

It was clearly evident during the electron-microscope investigation of the altered tuffs that the smectites composing the incrustate rims are well crystallized in contrast to those directly replacing the glass, have larger dimensions (on the order of $2 \cdot 10^{-5}$ mm), and have a foliaceous shape (Fig. 3a). Large segregations of zeolites coincide with the cavities (Fig. 3b).

The chemical compositions of the tuffs are presented in Table 1. In comparison with the chemical composition of the crystalline, relatively weakly altered basalts, the tuffs are characterized by lowered contents of SiO_2 , Al_2O_3 , CaO , Na_2O , and elevated contents of Fe_2O_3 , K_2O , and H_2O . Thus, the manifest trend in the chemical transformation of the tuffs resembles the process of palagonitization of sideromelane glass which takes place under marine conditions.

The phases and chemical compositions of the newly formed minerals were analyzed in samples 1056/3, 1058/6, and 1070/6. The pale-green clay mineral replacing glass is a dioctahedral ($d_{060} = 1.501$ Å) mixed-layer laminated silicate of the smectite-micaceous type containing approximately 40% layers of the micaceous type (Fig. 4). This follows from a comparative analysis of the diffractograms. In the untreated samples, $d_{001} = 11.82$ Å; in samples saturated with ethylene glycol, d_{001} increases to 16.55 Å, and one weak reflection $d_{002} = 9.61$ still appears, manifesting as a shoulder on the preceding peak; in the heated sample, $d_{002} = 9.78$ Å. Zeolites with a small admixture of cementing material were removed from sample 1058/3 for x-ray phase analysis. On the diffractogram, phillipsite and one of the varieties of apatite were identified as either francolite or dernite (Fig. 5a). On the diffractogram of sample 1070/6, potassium feldspar (see Fig. 5b), which replaces plagioclase microclites in this case, was identified along with smectite ($d_{001} = 13.60$ Å).

The chemical composition of the smectite replacing the glass (see Table 2, X, XII) and forming the incrustation (see Table 2, XI) was investigated with the aid of a microprobe. The analyses obtained were similar to one another; only the analysis of X differed significantly in having a high SiO_2 content. The smectite essentially has a ferroaluminosilicate composition. By recasting the analysis into a crystallochemical formula for 22 negative charges according to the standard methodology, by assuming that the iron primarily occurs in the oxidized form (which follows from a bulk chemical analysis of the rocks, and by taking the x-ray data into account), one can show that these minerals can be classified as ferruginous beidellite-glaucanites [1]



The chemical composition of the massive green clay mineral in sample 1070/6 forming sparse circu-

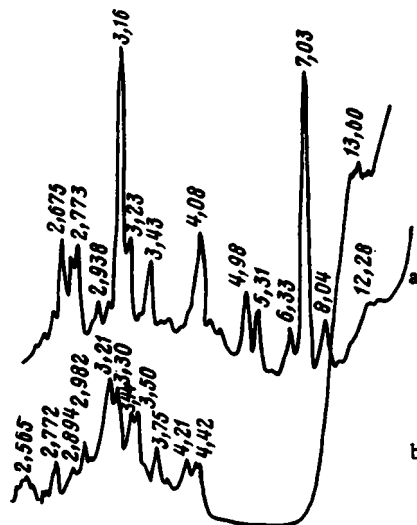


Fig. 5. Diffractograms of phillipsite (a) and potassium feldspar (b) (sample 1070/6).

lar features of up to 0.1-mm diameter on the converted glass was investigated (see Table 2, XIII). When the composition was recast into the crystallochemical formula of a clay mineral for 22 negative charges, it turned out to be similar to the composition of ferruginous saponite (when conditionally assuming $\text{Fe}^{3+}/\text{Fe}^{2+}$ to equal 3:1).



Thus, we have established the following association of secondary minerals formed during the conversion of the tuffs: ferruginous beidellite-glaucanite, phillipsite, potassium feldspar, iddingsite and ferruginous saponite. Most probably, they were formed during hydrothermal conversion of the tuffs. The following facts can serve as the basis for such an assumption: the universal transformation of the tuffs, the manifestations of hydrothermal processes in the basalt horizons, and the proximity of the ferruginous beidellite-glaucanite replacing the vitreous fragments to iddingsite formed in the basalts during the hydrothermal stage. The principal difference between these minerals consists in the lower Fe^{3+}/Al value in the beidellite-glaucanite. This is apparently due to the fact that the latter inherited, to some degree or another, the composition of the primary phase (sideromelane or palagonite) relatively enriched in aluminum.

Silty Clays. All of the samples of this rock had identical textures. Sparse silt-sized (~0.01-0.05 mm) grains of plagioclase (3-5%), iddingsitized olivine (2-4%), and ore mineral (up to 7%) are immersed in the ground/mass of a grey, finely dispersed clay mineral which is weakly doubly refractive. The fragmental fabric of the entire rock can be seen during examination with the electron microscope (see Fig. 3c). At the same time, the individual particles are composed of a very finely dispersed, foliaceous clay mineral analogous in morphology to the transformed tuffs.

On the basis of composition and structure, these rocks can thus be considered transformed ash deposits.

The dominant phase on the diffractograms of these samples is a dioctahedral ($d_{060} = 1.50$ Å) mixed-layer mineral of the smectitic-micaceous type ($d_{001} = 12.11$ Å in untreated samples, $d_{001} = 17.34$ Å and $d_{002} = 9.23$ Å in samples saturated with glycerine, and $d_{001} = 9.85$ Å in heated samples) containing approximately 30% micaceous layers.

The chemical compositions of the silty clays are presented in Table 1. They are similar in composition to altered tuffs, being distinguishable by their higher values of SiO_2 , MgO , and K_2O , and differing from samples of relatively weakly altered basalts by having low CaO and Na_2O content and elevated K_2O and H_2O content.

The results of the chemical and x-ray investigations of these rocks indicate that the clay mineral (the principal rock-forming mineral) is similar to that which is developing from the tuffs (i.e., similar to ferruginous beidellite-glaucanite).

Generalizing from all of the data on the silty clays, we arrive at the conclusion that these are ash deposits predominately composed of ferruginous beidellite-glaucanite which was formed during the hydrothermal conversion of vitreous fragments.

Sandstones. All of the sandstones encountered (samples 1069/2, 3, 9) have an identical texture and composition and can be classified as possessing fine to intermediate grain size. They are composed of detrital rounded, and semirounded grains possessing dimensions of 0.2-0.25 mm and good sorting. With respect to composition, these can be considered oligomictic sandstones. Approximately 70% of the fragments are represented by slightly porous (5-10%, with pore dimensions of 0.01-0.1 mm) basaltic glass, sometimes containing plagioclase microlites. The glass and microlites are replaced by greenish and yellowish-brown, very weakly birefringent smectite. Approximately 5% of the glass fragments are fresh. The remaining portion of the grains are represented by titanite (5-8%), iddingsitized olivine (10-15%), and plagioclase partially replaced by smectite.

The cementation of the sandstones is very weak and is represented by several types: the contact type, the pellicular type, and a type involving infilling of the pores. The intergranular space is filled with carbonate-phosphate material, but many of the pores remain empty. Benthic forms of foraminifera which, according to Kh. M. Saidov, have a Maastrichtian age, can be detected in the cement.

Thus, the sandstone is a result of basalt decomposition, predominately decomposition of vitreous quenched crusts. Apparently, the disintegration of the basalts and the formation of the sandy deposits occurred under the action of marine abrasion in a time when the upper portion of the volcanic structure was located above sea level.

The chemical composition of the sandstones (see Table 1) is characterized by relatively high contents of CaO and P_2O_5 as a consequence of the comparatively large quantity of carbonate-phosphate cement. The same features are present in the rest of the chemical composition of the sandstones that we find in vitroclastic tuff.

Essentially, we can identify a single phase on the diffractograms of sandstones purified of carbonate-phosphate cement; this is a dioctahedral ($d_{060} = 1.501 \text{ \AA}$) mixed layer, very disorganized clay mineral of the smectitic-micaceous type (basal reflection at 12.11 $\text{\AA}$ in the untreated samples, 17.64 and 10.05 $\text{\AA}$ in the sample saturated with glycerine, and 9.89 $\text{\AA}$ in the heated sample).

Judging from the calculated data (when sandstones of an apatite composition are subtracted), the chemical composition of the clay mineral (the primary mineral of the sandstones) is similar to the composition of ferruginous beidellite-glaucanite.

Turbidites. The rocks which we have combined together in this group according to textural criteria have identical compositions (samples 1065/1, 3, 4), with the exception of sample 1065/2. They are composed of slightly rounded fragments of isometric and tabular forms of vitroclastic tuff with psephitic (sample 1065/1) and psammitic (samples 1065/3) dimensions. In sample 1065/4, these fragments form rhythms with gradational layering. Three rhythms of 3-10 cm thickness can be detected. In each rhythm, the dimensions of the fragments of altered tuff vary from 1-1.5 cm to silt-sized dimensions on the top. Samples 1065/1-3 are apparently also separate elements in a rhythm of turbidite deposits.

Practically all of the tuff fragments are replaced by light-green finely dispersed smectite; some of the fragments contain iddingsitized phenocrysts of olivine. The tuff is very porous (25-30%), the pore dimensions are 0.25-5 mm). The pores have an incrustate ring of light-green smectite. The nuclei of some of the pores are filled with calcite. In sample 1065/1, the very common fragments unevenly distributed throughout the volume of the sample are fresh vitroclastic tuff. This fact indicates that the turbidites were not altered at their place of occurrence but were formed from already converted tuffs.

The cementation of the fragments is very weak and uneven; the cements of the pellicular and basal types are represented by calcite and, more rarely, phillipsite. The samples crumbled during drying; consequently, they could not have been transported long distances in the form of such large blocks.

The electron-microscope investigation of individual tuff fragments indicated that they were composed of well-crystallized smectites of foliaceous shape (see Fig. 3d). According to the data of x-ray diffractometry, the clay mineral is a dioctahedral ($d_{060} = 1.501 \text{ \AA}$) smectite (the basal reflections are: 13.03 $\text{\AA}$ in the untreated sample, 19.36 and 9.21 $\text{\AA}$ in the sample saturated with glycerin, and 9.89 $\text{\AA}$ in the heated sample).

The chemical compositions of rocks (see Table 1) purified of carbonate cement are similar to the chemical compositions of the altered vitroclastic tuffs, differing somewhat

in their higher values for TiO_2 and H_2O , and their lower values for K_2O . The crystallochemical formula of sample 1065/3 corresponds to dioctahedral smectite similar to the ferruginous beidellite-glaucanite from samples 1058/6 and 1070/6:



Sample 1065/2 has a fragmental texture and is composed of practically single grains of apatite of silty (~0.01 mm) dimensions. Approximately 2-3% grains of plagioclase and 1-2% of the fragments of volcanic glass were noted. We identified only one phase on the diffractogram of the sample, this phase was recognized, on the basis of a set of reflections, as one of the varieties of apatite: either dernite or fracolite (3.43, 3.16, 3.04, 2.768, 2.675, 2.616, 2.495, 2.23, 2.12, 2.05 Å).

The presence of phosphate interlayers is additional evidence that these turbidites are sedimentary formations. Their origin was apparently associated with the breakdown of the carbonate-phosphate cement in the tuff deposits.

Thus, the turbidites are a result of the decomposition of unconsolidated strata of altered vitroclastic tuffs weakly cemented with carbonate-phosphate material.

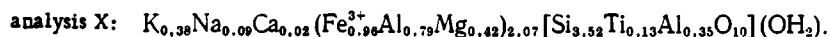
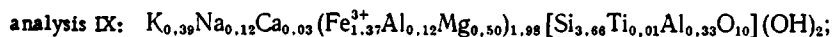
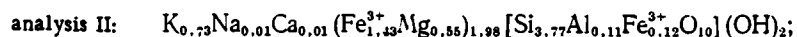
Breccias. The breccias can be mono- or polymictic. The first type are composed of irregularly angular fragments of basalts (from 2 to 20 cm). There may be basalts, tuffs, and limestones (samples 1056/2, 4, 1057/4, 1070/8) within the composition of the more common polymictic breccias.

The cement of the breccias is sandy-carbonate-phosphate. In the carbonate-phosphate material (resulting from a phosphatization of limestone foraminifera deposits), approximately 15-20% of the rounded and unrounded grains of sandy dimensions (0.1-1 mm), represented by strongly altered crystalline basalts, altered basaltic glass, and tuffs, are fused.

Planktonic foraminifera dating from Paleocene to late Miocene can be detected in the cement of the breccias, according to the determinations of Kh. M. Saidov.

We can arrive at the following conclusions on the basis of the material presented. The tops of the volcanic sections of the Ita Mai Tai and IOAN guyots are composed of interstratified horizons of subalkaline basalts and vitroclastic tuffs. All of the volcanogenic rocks were hydrothermally reworked, with the tuffs being reworked most intensely (this was due to their good permeability and reactivity). The principal newly formed minerals arising during the hydrothermal stage in the conversion of the volcanites were dioctahedral smectites and mixed-layer minerals of the smectite-ferruginous mica type. They constitute completely the vitroclastic tuffs and also the vitreous crusts of the basalts and are represented by ferruginous beidellite-glaucanite. In the crystalline basalts, it is nontronite which settles into the pores and veins and replaces olivine and plagioclase.

The newly formed dioctahedral layered silicates were: glaucanite, nontronite, and ferruginous beidellite-glaucanite: they form an authigenic series on the basis of their crystallochemical features:



A sequential increase in the content of Al and Ti, along with a decrease in the content of octahedral Fe^{3+} and a disappearance of its tetramers, can be detected. From glaucanite to nontronite, there is a significant increase in the quantities of Na and Ca in the interlayers; the quantities of Na and Ca drop somewhat again at the transition to beidellite-glaucanite. The peculiarities in the behavior of the petrogenic elements apparently reflect the compositions of the primary phases and conditions of mineral formation. During the post-eruptive stage (taking place instantaneously from the point of view of geological time), the most stable ferromagnesian phases (olivine) were broken down. During the hydrothermal stage, the primary reactive material was the quenched glass of the basalts and vitroclastic tuffs. During this stage, all of the elements were mobilized to one degree or another, and, therefore, the nontronite, which precipitated out of solutions mineralized chiefly by material partially leached from the tuffs is, in comparison with glaucanite, enriched even with such relatively poorly mobilizable elements as Al and Ti, and especially with the most leachable elements,

such as Ca and Na. Correspondingly, the minerals directly replacing the glass are, in comparison with nontronite, enriched substantially with the least mobile elements, Al and Ti.

The distribution of clastic rocks on the slopes of the guyots is evidence of above-water and submarine physical decomposition of basalts and tuffs. Massive basalts breaking down during marine abrasion formed breccias, and their most altered varieties, most importantly the vitreous altered zones of flows and pillows, participated in the cementation of the breccias when they disintegrated to gravelly and sand dimensions.

The fact that the basalts form positive morphostructures on the ocean floor was conducive to their physical breakdown under submarine conditions. Massive basalts which broke down during marine erosion formed breccias; the more altered varieties of the basalts, most importantly vitreous altered zones of flows and pillows disintegrated to gravelly and sandy dimensions, played a role in the cementation of the breccias.

We have suggested that the turbidites taken from the slopes of the IOAN guyots were formed as a result of the decomposition of tuffaceous deposits and represent sedimentary formations. The following facts can be cited in favor of this: criteria associated with the degree of rounding of the grains, the presence of phosphate interlayers, and the combination of altered and unaltered tuff fragments in single lumps. This contradicts a tuffaceous origin for these turbidites. Moreover, the absence of a ferromanganesian crust on the lumps indicates that the lumps were formed relatively recently, since volcanism in this region ended during Cretaceous times.

At this point in the investigation, it is consequently most reasonable to suppose that the turbidites which we studied were formed as a result of precipitation from turbid flows transporting the decomposition products of tuffaceous deposits. The mechanism of creation for these turbid flows is, in the end, unclear. Possibly, the presence of horizons of strongly altered but weakly cemented tuffs, which, in the event of their decomposition, could concurrently tie up large volumes of material, is an important prerequisite for the generation of such flows.

During the breakdown of the intercalations of altered ash, clay pellets were created and formed accumulations on the gentle areas of the slopes.

The most abundant mineral in all the clastic rocks found on the slopes of the guyots, with the exclusion of the breccias, is ferruginous beidellite-glaucinite. When investigated chemically and by x-ray photography, it turned out to be similar in composition and structure to various clastic rocks. This was due to its formation as a result of hydrothermal conversion of the quenched glass which chiefly composed the horizons of vitroclastic tuffs and the subsequent decomposition of these strata.

With respect to the crystallochemical features, the ferruginous beidellite-glaucinite is especially similar to the ferruginous smectites widely distributed both in modern red clays and in the more ancient sedimentary rocks containing clay minerals in the first layer of the ocean crust [1, 2]. The higher content of titanium in the beidellite-glaucinites is an important difference; this is a reflection of the alkaline-basaltic composition of the primary rocks.

LITERATURE CITED

1. V. A. Drits and A. G. Kossovskaya, "Geocrystallochemistry of rock forming dioctahedral smectites," *Litol. Polezn. Iskop.*, No. 1, 84-114 (1980).
2. A. G. Kossovskaya, E. B. Gushchina, V. A. Drits, et al., "Mineralogy and genesis of Mesozoic-Cenozoic deposits of the Atlantic Ocean according to data of the 2nd voyage of the Glomar Challenger, *Litol. Polezn. Iskop.*, No. 6, 12-36 (1974).
3. A. G. Kossovskaya, I. M. Simanovich, and V. D. Shutov, "Mineral conversions of rock in the oceanic crust and the problem of its initial continentalization," *Mineral conversions of the Rocks of the Oceanic Substrate* [in Russian], Nauka, Moscow (1981), pp. 5-16.
4. V. B. Kurnosov, *Hydrothermal Alterations of the Basalts in the Pacific Ocean and Metaliferous Deposits* [in Russian], Nauka, Moscow (1986).
5. S. G. Skolotnev, "Mineral formation during the oxidation of the iron in the basalts of the Klyuchevsk group of volcanoes," *Izv. Akad. Nauk SSSR, Ser. Geol.* No. 4, 65-74 (1984).

EDAPHOGENIC MATTER IN SEDIMENTS OF THE NORTHERN TROPICAL ZONE OF THE ATLANTIC OCEAN

V. N. Sval'nov, N. V. Belyaeva,
O. B. Dmitrenko, Z. T. Novikova,
T. Yu. Uspenskaya, and A. Ya. Shevchenko

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Tectoedaphogenic and bioedaphogenic substances have been identified by a variety of methods in concretion cores and sediments along a section that crossed the Guiana Basin–North Atlantic Ridge–Canary Basin area. Evidence of repeated tectonic activity along the Kane Fracture Zone during the Pleistocene has been established and hydrothermal alteration of sedimentary rocks described in the Guiana Basin.

In Petelin's genetic classification [3] of genetic categories of deep water sediment components, lithogenic marine disintegration products from the submarine lithosphere (ocean floor) play an important role. They were named edaphogenic components. These components, established during mineralogical studies of sandy-silty sediment fractions, are widespread in various structural-facies zones of the World Ocean. These are taken into account not only during mineral identification [2, 5, 8, 9] but in identifying genetic categories of oceanic deposits [1, 4, 6]. Presently, we offer results of complex studies on tecto- and bioedaphogenic sediment components. The tectonic components are marine endolithogenic products of tectonic rock disintegration (crushing), the other category consists of fossil organisms separated during exogenic disintegration of sedimentary rocks [3] and differing degrees of sediment lithification [6]. Tectonic disintegration products of rocks and bioedaphogenic fragments often form the nuclei of Fe–Mn concretions. For this reason, in the following we briefly discuss also the formation and composition of the concentric shells in ore concretions.

The samples for this study came from nuclei of Mn–Fe concretions and size fractions of sediments from the northern tropical Atlantic Ocean, taken during the 40th cruise of research vessel Academician Kurchatov in 1984. Samples were collected at 2900–6006 m depths of the Guiana Basin, on slopes of the North Atlantic Ridge and its transitional zone toward the Canary Basin, close to the Kane transform fault system (Fig. 1). Age determination was based

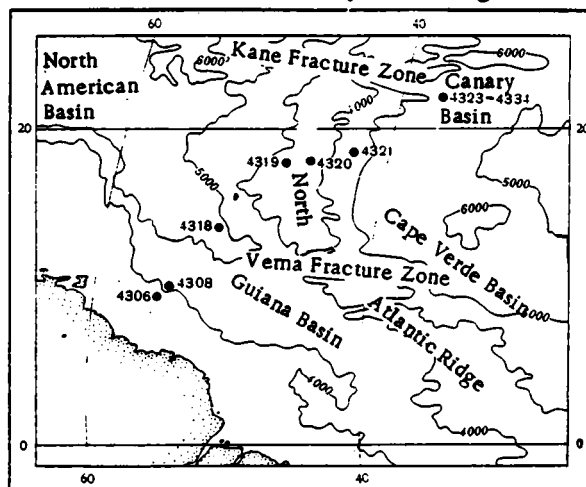


Fig. 1. Station locations. Solid dots: sediment and concretion sample locations; isobath values in meters.

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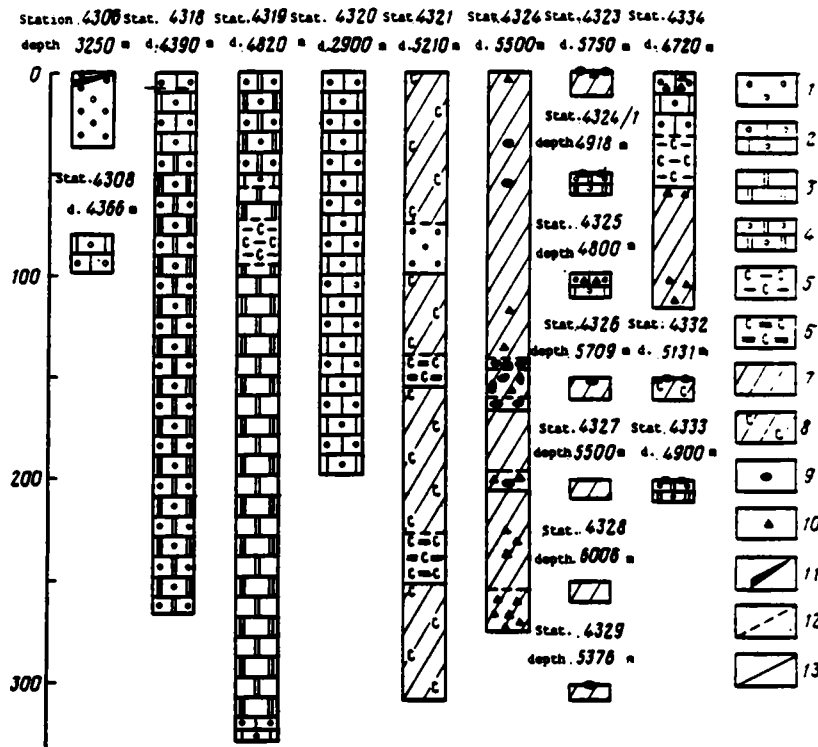


Fig. 2. Lithology of dredge samples and cores. 1-6: sediments (1 - foraminifer-bearing; 2 - coccolithic-foraminifer-bearing; 3 - coccolithic; 4 - foraminifer-bearing-coccolithic; 5 - clayey-limey; 6 - limey-clayey); 7 - miopelagic clays; 8 - same, slightly limey; 9-10 - Mn-Fe concretions (9 - rounded; 10 - angular-shaped); 11 - Mn-Fe crusts; 12-13 - subdivision boundaries (12 - gradual; 13 - abrupt boundary).

on coccolithophore and planktonic foraminifer assemblages. Diffractometer DRON-2 with $\text{CuK}\alpha$ -emission was used in x-ray analysis. An Ni-filter was employed with 40 kV and 20 mA current and 0.5×0.5 mm aperture. A JSM-U3 scanning electron microscope was used. Polished sections of ore concretion shells were studied in reflected light. Total silicate analyses of the sediments were conducted by the VRA-2 x-ray apparatus by M. M. Kakhan and T. G. Kuz'min. Atomic-absorption spectrophotometer AAS-403 was used in determining Fe, Al, Cu, Sr, Mn, Ni, Co, Zn, Ti, Mo, Pb, V, Mg, Ca, Li, Cr, and Cd in acetylene-air + acetylene-nitrous oxide flame by N. N. Zavadskaya. The gas-volume express method of Knopp was employed by N. P. Tolmacheva in analyzing CO_2 and organic carbon. Sections of concretion nuclei found in metamorphic and igneous rocks were studied by G. L. Kashintsev. The grain-size distribution of the samples and interrelationship of minerals in the coarse silt sediment fractions were determined by members of V. P. Kazakova's study group.

Direct-flow tubing was used to penetrate the mostly Pleistocene-Holocene muds in the study area. At depths less than 4900 m oxidized biogenic carbonate sediments occurred with foraminifer, coccolithic-foraminifer, and foraminifer-coccolithic composition. Miopelagic clays, locally of slightly limey composition occurred between 5100-6000 m (Fig. 2). At station 4306 (Guiana Basin) trawl samples from the 3310-4120-m depth interval included chunks of clayey limestones of coccolithic-foraminifer composition, while cores recovered limey, slightly consolidated matter of similar composition. The limestones were covered by glossy (smooth) or hummocky-surfaced Fe-Mn crust, 0.5-0.8 cm thick and penetrated by numerous borings of burrowing organisms. The burrows ranged between fractions of a millimeter to 3-4 cm in diameter and often were filled by younger sediments. The burrow walls usually were covered by a 1-3-mm-thick film of Fe- and Mn-hydroxides. In addition to these limestones, individual ellipsoidal-shaped iron concretions and angular fragments of strongly altered yellowish-brown argillites and brownish-green clayey limestones were also found in the dredge sample. Fe-Mn-bearing fringer also occurred on the fragment surfaces ("immature" concretions). The maximum 3-mm-thick ore crust also occurs in cores of weakly consolidated foraminifer-dominated

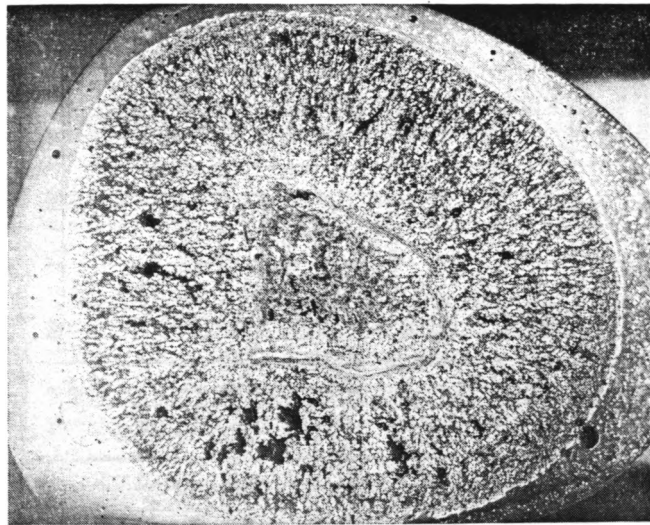


Fig. 3. Radial-dendritic structure of ore-bearing concretion shell. Polished section, 1.8× magnification.

sediments in station 4306 (Fig. 2).

Numerous concretions cover sediments in the Canary Basin area (stations 4323-4334). In addition to rounded concretions, with ore shells maximum 2.5 cm thick, "immature" and probably younger concretions are also common there. Their outline follows the angular concretion core outline and their ore crust is only 1-3 mm thick. A concentration of angular concretions at station 4334 also occurs in the subbottom sediment layers. Such concretions are especially numerous in the core of station 4324 where they are dispersed in the sediment bed and form three horizons with the rounded concretions (140-165, 196-206, and 253-273-cm intervals). The long concretion axes often are oriented close to the vertical. The combination of this circumstance with the burial of concretions of various stages of maturity at the same time apparently indicates the possibility that the concretions were redeposited during a number of depositional cycles. Proof of the redeposition of finer (bioedaphogenic) matter may be found in sediment core of station 4321: miopelagic clays here include limey (foraminifer-dominated) turbidites (Fig. 2).

Characteristics of Concretion Ore Shells. Spherical, ellipsoidal, and compressed varieties are found among the rounded concretions. Their surfaces are smooth along their total perimeter. The cores are composed of clayey matter and partially replaced by Fe- and Mn-hydroxides. The surrounding ore-bearing shell is 1.0-2.5 cm thick. The ore crusts are characterized by quite uniform composition between the core and their surface between their lower and upper bounding surfaces, as manifested by the development of a radial-dendritic structure (Fig. 3). The structure formed through the growth of dendrites, elongated parallel with the concretion radii. Each dendrite has a laminated structure, expressed in the alternation of poorly reflective isotropic ore layers (crossed nicols) with very thin black clayey laminae. The interstices between the dendrites are filled by detrital nonore matter that occurs in significant amounts close to the concretion nuclei. Practically all the studied concretions possess a texturally uniform ore shell in the near-core and near-surface areas. The thin (maximum 1 mm) shell has a finely-laminated structure, composed of alternating gray (in reflected light), light gray, anisotropic ore and black clay laminae.

Based on earlier mineral studies on concretions from this area by analytical electron microscopy (electron microdiffraction and energy-dispersive microprobe analyses [10]), the basic ore-forming minerals in the iron-rich concretions ($Mn/Fe < 1$) with radial-dendritic ore-shell structure are represented by Fe-vernadite and ferroxigite that occur together in ultrafine interpenetration. The concretions also include admixtures of goethite, low-iron vernadite and disordered mixed-layer asbolite-buzerite. Increased concentrations of the dominantly Mn-phase occur only in the finely-laminated zones where they occur in more high reflective anisotropic layers. As known [15], these are enriched in Mn, Ni, and Cu. The Mn-rich, anisotropic matter forms not only individual layers but also fills fractures and partially interstices between dendrites, extending into an earlier formed radial-dendritic shell.

TABLE 1. Chemical Composition of Concretions and Ore-Bearing Crusts

Sample number	Depth, m	Sample type†	Fe	Al	Cu	Sr	Mn	Ni	Co	Zn	Ti	Mo	Pb	V	Mg	Ca	Li	Cr	Cd	Mn/Fe	Composition of substances or strata of ore-bearing crusts
4306/9	3310—4120	S	20,56	2,54	0,04	0,024	2,11	0,03	0,026	0,041	0,43	0,003	0,068	0,087	1,08	0,59	17	40	9	0,10	Clay
4306/2	4120	OC	17,32	3,02	0,03	0,071	7,23	0,07	0,072	0,028	0,35	0,015	0,043	0,072	1,05	2,24	15	22	8	0,42	Clayey limestone
4306/3	4120	OC	15,64	2,85	0,04	0,076	10,24	0,19	0,104	0,030	0,43	0,022	0,047	0,065	1,22	2,22	17	29	8	0,66	Same
4306/4	4120	OC	19,66	3,34	0,13	0,083	14,16	0,22	0,397	0,044	0,77	0,030	0,070	0,064	1,40	1,51	12	47	12	0,72	»
4323/1	5750	S	14,42	2,82	0,03	0,065	6,92	0,12	0,067	0,025	0,33	0,015	0,037	0,061	1,12	2,40	15	26	7	0,48	Olivine gabbro
4323/2	5750	S	19,66	3,09	0,23	0,073	16,87	0,37	0,345	0,054	0,76	0,035	0,091	0,070	1,71	1,36	102	52	15	0,86	Clay
4324/1	4918	U	20,11	2,43	0,11	0,104	16,87	0,22	0,474	0,044	0,91	0,033	0,099	0,070	1,36	1,79	12	31	10	0,84	Tremolitized and chloritized peridotite
4324/2	4918	L	18,88	2,41	0,12	0,104	17,46	0,20	0,465	0,043	0,91	0,029	0,095	0,062	1,27	2,28	12	24	12	0,93	Same
4324/3	4918	S	18,44	2,73	0,12	0,085	14,03	0,23	0,391	0,044	0,79	0,029	0,081	0,061	1,32	1,71	11	43	10	0,76	Serpentinite
4324/4	4918	S	18,33	2,18	0,09	0,114	18,75	0,29	0,467	0,041	0,80	0,030	0,098	0,071	1,40	2,42	7	14	12	1,02	Same
4324/5	4918	U	19,89	2,65	0,12	0,091	14,45	0,22	0,395	0,043	0,84	0,030	0,098	0,077	1,41	1,69	15	27	10	0,73	Weathered apoperidotitic serpentinite
4324/6	4918	L	18,55	2,41	0,12	0,090	14,75	0,24	0,400	0,042	0,86	0,026	0,092	0,064	1,33	1,90	12	26	11	0,80	Same
4324-157	5500	NS	18,33	3,22	0,21	0,061	16,26	0,39	0,307	0,051	0,70	0,049	0,071	0,060	1,80	1,27	87	103	12	0,89	Uralitized leucogabbro
4332/25	5131	S	18,77	3,22	0,14	0,075	14,45	0,30	0,351	0,045	0,74	0,028	0,080	0,098	1,62	1,69	40	55	12	0,77	Uralitized olivine gabbro
4333/1	4900	U	20,78	2,73	0,24	0,068	14,45	0,41	0,350	0,055	0,98	0,030	0,092	0,075	1,82	1,32	67	22	13	0,70	Clay
4333/2	4900	L	20,33	2,93	0,22	0,054	12,65	0,39	0,310	0,054	0,87	0,025	0,074	0,074	1,76	1,09	72	31	13	0,62	Same
4333/3	4900	S	18,55	3,14	0,18	0,071	14,45	0,39	0,345	0,049	0,70	0,031	0,076	0,062	1,69	1,38	52	58	10	0,78	»

*Li, Cr, and Cd content given in $n \cdot 10^{-4}\%$, remaining elements in percentage.

† S—av. sample of surficial concretions; NS—av. sample of buried near-surface concretions; U—upper portion of unburied concretions; L—same, lower portion; OC—av. sample of ore crust.

TABLE 2. Chemical and Granulometric Sediment Composition (% dry weight)

Sample No.	Sedi- ment type*	SiO ₂	TiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MnO	MgO	CaO	K ₂ O	Calcin. loss	Or- ganic carbon	CaCO ₃	Size fraction, in mm			0,25-0,1†	0,1-0,05 †
													>0,1	0,1-0,01	<0,01		
4306/3	CFCL	13,9	0,15	3,7	1,5	0,05	0,7	39,7	0,73	36,4	0,56	57,70	18,45	18,63	62,92	0,03	0,01
4306/4	»	21,8	0,19	4,8	6,5	0,05	0,8	29,4	1,00	31,9	0,26	49,30	28,22	6,69	65,09	0,01	0,01
4306/5	LC	31,8	0,56	13,6	5,1	0,12	0,7	18,4	2,20	24,4	0,43	30,81	1,02	5,67	93,31	0,48	0,02
4306-0-5	F	14,0	0,14	4,9	0,8	0,05	0,6	38,8	1,00	36,8	0,22	71,00	33,86	14,11	52,03	0,03	0,03
4306-5-10	»	12,2	0,13	3,3	1,5	0,05	0,6	45,1	0,54	33,3	0,38	74,10	23,71	11,51	64,78	0,03	0,03
4306-20-25	»	9,4	0,09	3,0	0,9	0,07	0,6	44,0	0,49	38,6	0,43	76,60	30,08	13,97	57,95	0,01	0,01
4306-32-37	»	10,4	0,11	3,2	1,1	0,04	0,6	42,1	0,57	38,7	0,39	73,50	28,96	21,35	49,69	0,03	0,03
4323-0-2	MC	47,9	1,07	19,9	7,2	0,55	3,5	0,5	1,91	14,4	0,46	0,16	0,18	0,66	99,16	—	2,49
4323-7-12	»	46,4	1,04	19,2	6,7	0,47	4,0	2,9	1,80	14,4	0,23	7,80	5,43	1,00	93,57	1,19	0,34
4324-1-0-2	CF	16,1	0,35	5,2	2,1	0,10	0,7	37,0	1,20	35,0	0,26	67,20	13,85	14,01	72,14	—	0,04
4324-3-5	»	12,6	0,25	4,2	1,6	0,07	0,7	39,7	1,40	36,6	0,19	71,60	21,87	13,55	64,58	0,04	0,01
4324-0-5	MC	49,5	0,99	18,1	6,7	0,51	4,4	0,7	2,00	14,1	0,25	5,80	0,32	1,50	98,18	—	0,75
4324-15-19	»	47,8	0,92	19,1	6,5	0,50	3,5	4,2	2,00	12,3	0,12	1,13	0,28	0,14	99,58	2,35	0,75
4324-40-45	»	47,9	1,05	19,6	7,1	0,46	3,4	3,2	1,90	12,3	0,14	0,81	0,20	0,90	98,90	6,35	0,73
4324-90-95	»	51,6	1,00	18,4	6,9	0,48	3,4	0,6	2,30	12,1	0,08	0,25	0,47	0,46	99,07	2,76	1,84
4324-110-115	»	50,7	0,83	19,4	6,6	0,52	4,8	0,4	1,70	12,3	0,05	0,25	1,27	1,00	97,73	3,78	0,57
4324-120-125	»	52,5	1,07	20,6	7,4	0,56	3,0	0,5	2,50	9,0	0,07	0,16	0,79	0,53	98,68	3,34	0,48
4324-135-140	»	56,6	1,15	16,0	7,2	0,56	2,8	0,7	2,60	8,9	0,05	0,07	1,17	0,49	98,34	3,16	2,44
4324-147-152	»	56,8	0,59	17,7	6,9	0,53	2,5	0,5	2,60	8,8	0,05	0,16	3,82	0,61	95,57	1,51	0,41
4324-177-182	»	55,2	1,01	17,2	6,9	0,60	2,9	0,1	3,10	9,5	0,07	0,09	1,42	0,51	98,07	4,58	2,65
4324-196-201	»	53,9	1,00	14,2	7,0	0,58	2,0	0,6	2,80	14,4	0,05	0,25	2,83	0,65	96,52	5,76	1,16
4324-206-211	»	50,6	0,96	15,2	6,7	0,73	3,5	1,1	2,50	15,6	0,09	0,09	1,28	0,64	98,08	6,05	0,79
4324-230-235	»	49,4	0,74	13,6	5,8	0,66	7,1	0,9	1,80	17,8	0,08	0,09	0,79	0,85	98,36	—	7,97
4324-248-253	»	49,2	0,84	14,1	6,2	0,66	6,0	0,6	1,40	17,9	0,11	0,34	0,78	0,52	98,80	11,49	4,08
4324-263-268	»	51,2	0,91	15,3	7,4	1,00	5,4	1,4	2,10	12,9	0,11	0,50	4,74	1,37	93,89	12,25	3,04
4333-0-3	CF	17,0	1,30	5,6	2,0	0,09	0,7	35,6	1,20	33,5	0,29	61,70	9,19	17,40	73,41	—	0,03
Pacific ocean	MC(P)	51,7	0,64	13,0	7,41	0,81	4,7	1,62	2,32	15,0	0,27	—	—	—	—	—	—

*CFCL-coccolithic-foraminifer-bearing clayey limestone; LC-limey-clayey sediment; F-foraminifer-bearing sediment; MC-miopelagic clay; CF-coccolithic-foraminifer-bearing sediment; MC(P)-miopelagic clay, Pacific Ocean (average of 17 samples) [7].

†Heavy mineral content in the fraction.

Apparently, this indicates influences of such solutions on the concretions that were enriched Mn, diagenetically mobilized from the sediments. The small volume of finely laminated zones suggests that the diagenetic processes apparently were of short duration and of quite low intensity but the groundmass of the ore shell that consisted of fine-grained ferroxigite and Fe-bearing vernadite, formed by hydrothermal processes.

The chemical composition of the studied concretions and ore crusts is shown in Table 1. The compositional-genetic and morphological features indicate the presence of a depositional Fe-Mn (Canary Basin) and an iron-rich (Guiana Basin) concretion category. The Mn/Fe ratios range between 0.10-1.02 but this value is always somewhat lower in the upper portion of the concretions than in the lower portion. This suggests also a minor diagenetic influx of Mn from the sediments, as established in mineralogical studies. In addition to Fe-enrichment, the upper portion of the concretions is often enriched also in Co, Mo, Pb, V, and Mg, in contrast with the lower segment. A significant variation of the concretion composition values in the station 4323 dredge sample may be explainable by their different ages and the differences in the mechanical growth of concretions of different morphologies. The compressed concretions are in very extensive contact with diagenetically active sea-floor surface sediment layers and are more significantly influenced by metal (mostly Mn) influx to the concretion ore shell from muddy waters than are the rounded (ellipsoidal) concretions. Actually, greatly compressed (0.5 × 5.0 cm) concretion #4323/2 was enriched in most of the analyzed elements, in comparison with concretion #4323/1 but had a composition close to that of the relatively older, buried concretion #4324-157, found at 157-cm depth at station 4324. Comparison of concretions and ore crusts in the Guiana Basin (samples #4306/2-4, 9) indicates significant enrichment of crusts by Sr, Mn, and Co.

Tectosedaphogenic Substances in the Canary Basin. In general, concretion nuclei in the Canary Basin consist of igneous and metamorphic rocks (tectosedaphogenic matter); to a lesser extent of clayey sediments and shark teeth. 90 small (3-20 mm) rock fragments were studied in thin section. These consisted of peridotite (39%), gabbro (31%), dolerite (6%), and metamorphic rocks (24%). Among the metamorphics, those formed from peridotites dominated.

Three, structurally and alteration-wise interrelated rock groups have been identified among the peridotites: 1) almost undeformed, weathered serpentinites (apodunites and apoperidotites); 2) serpentinites, subjected to tectonic and hydrothermal alterations; 3) peridotites from the transitional zone, typical of a differentiated basite-ultrabasite complex (pyroxene-plagioclase peridotites and olivine pyroxenites). The presence of boudinage in the second group emphasizes the fracture system and the orientation of antigorite flakes. A mixed aggregate of talc and tremolite developed from serpentinite. Judging from the intensive boudinage formation and hydrothermal metamorphism, rock fragments of this group came from deformed rocks of the ophiolitic series, exposed in the fracture zone.

The gabbroids belong to two groups: 1) relatively weakly deformed rocks that retained their primary structure (medium- and coarse-grained gabbros and gabbro-pegmatites); 2) cataclastic rocks, crushed to different degrees. All gabbros are leucocratic, they clearly display dominant plagioclase and the pyroxene content occasionally reaches 40%. Plagioclase crystals are deformed in the coarse-grained gabbro, as shown by the mosaic-type extinction pattern and traces of grain crushing. Cataclastic features in the second gabbroid group are displayed by the bending and spalling of coarse plagioclase and pyroxene crystals and the beginning of crushing of minerals with the development of granoblastic aggregates, consisting of small (0.1-0.2 mm), rounded and isometric grains.

The dolerites consisted of 20-50% lathlike plagioclase crystals, selectively replaced by zeolite or ore matter. Isometric, columnar, and radial precipitates of brownish-green hornblende of transitional composition occur in the interstices. Sphene and leucoxene with amphibole occur typically in the dolerites.

More than half of the metamorphic samples contain monomineralic tremolite that formed from apoharzburgitic serpentinites. The serpentinite boudinage is outlined by one-directional tremolite crystal orientation and the pulling apart of ore mineral grains to form individual fragments of irregular shape. Certain samples consisted essentially of brownish-green actinolite or brown hornblende. In addition to metamorphosed peridotites, the concretion nuclei included individual fragments of leuco- and melanocratic gabbro that underwent greenstone alteration. Apparently, the gabbro has undergone intensive cataclastic changes and mylonitization in the zone of schist and boudinage formation. Relatively coarse clinopyroxene grains were found as individual relicts. They were partially replaced by tremolite

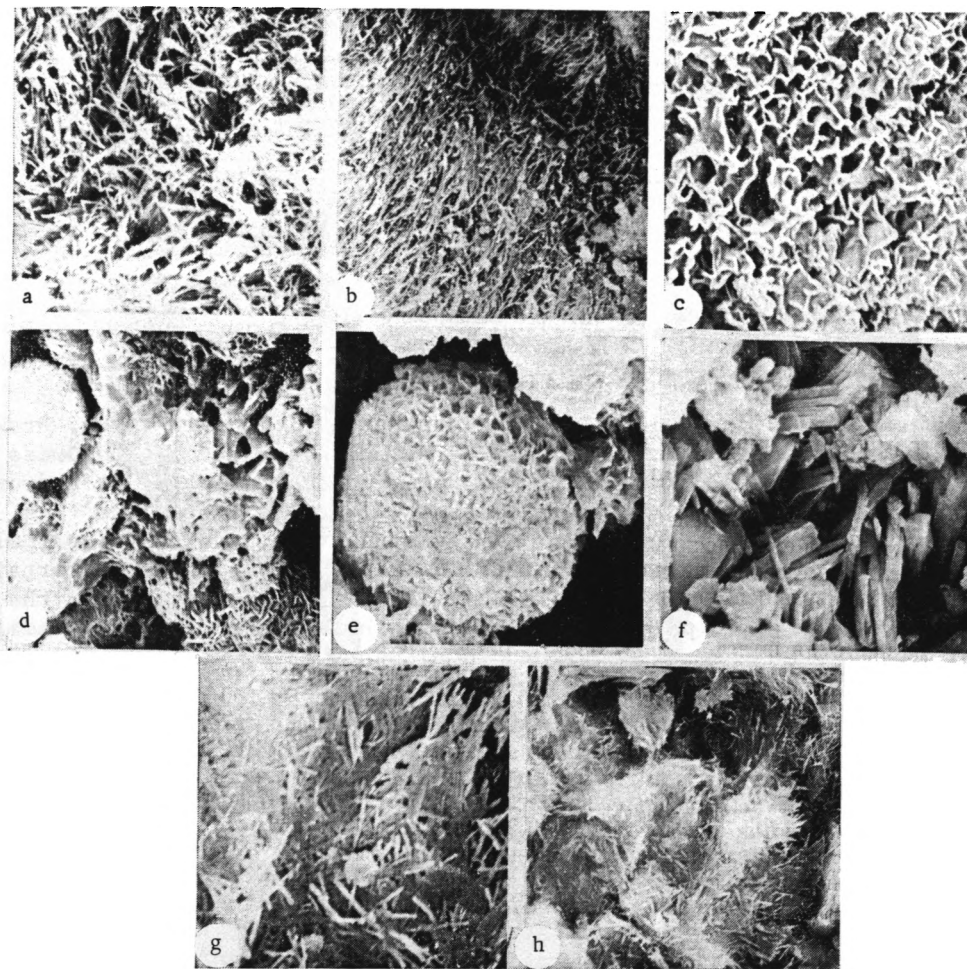


Fig. 4. Sediment composition of concretion cores (SEM images): a) chrysotile, 3000× magnification; b) antigorite, 1500× magnification; c) smectitic ground mass of core, 3000× magnification; d) spheroidal smectite variety, 2250× magnification; e) same, 3000× magnification; f) edaphogenic amphiboles, 2500× magnification; g) palygorskite, 5000× magnification; h) serpentinite fragments, 1500× magnification.

that occurs along with the slightly effected mass of that mineral. Lenticular layers of nematoblastic tremolite aggregates also occurred. Individual fragments among the collected metamorphic rocks consisted only of an almost monomineralic chlorite rock with leucoxene admixture. They probably formed from Ti-magnetic melanogabbro. In general, the metamorphic rocks consisted of greenschist, epidote-amphibolite and partially amphibolitic facies of progressive ophiolite metamorphism.

The apparent predominance of peridotites and gabbro among the studied rock fragments indicates that the seafloor area where the tectoadaphogenic matter originated contains deep rock types of the oceanic crust, formed on the seafloor in a tectonically active zone. If the Kane Transform Fault Zone that according to seismic data occurs at 24°N [20] reaches 22°N, then the investigated part of the Canary Basin occurs in an area of meridional faults, parallel with the axis of the Mid Atlantic Ridge rift valley and the southern edge of the Kane Fault Zone. This seems to be confirmed by the petrographic study of boudinage in concretion nuclei and cataclastic and deformation rock features, typical of fault zones. Fracturing itself is the basic factor in the mobilization of edaphogenic matter. Therefore, one may expect the sediments to display indications of components of decomposed deep rocks, such as ortho- and clinopyroxenes, hornblende, olivine, sphene, leucoxene, magnetite, Cr-spinel and zeolites.

In addition to the ophiolite rock association, the concretion cores in the Canary Basin also contained individual shark teeth and clay sediments with varying degrees of acquired

TABLE 3. Composition and Interrelationship of Concretion Cores in Drillhole Core #4324, %

Interval, cm	No. of concretion cores	Dolerites	Gabbroids	Meta-morphic rocks	Sediments
0-140	5	20,0	80,0	—	—
140-145	9	—	77,8	22,2	—
145-158	15	6,6	73,6	13,2	6,6
158-165	5	—	100	—	—
196-206	12	—	24,9	8,3	66,8
206-242	5	—	—	20,0	80,0
243-273	20	—	5,0	5,0	90,0

iron content (fragment size: 0.5-6.0 cm). The clays were of cinnamon-brown, brown, cinnamon-yellow and light-cinnamon colors. The finely dispersed sediment groundmass included numerous Mn-hydroxides dendrites, often elongated zones, also fringed by Mn-hydroxides. Occasionally small shark teeth, edaphogenic fragments of altered ultrabasites (Fig. 4a, b), quartz and feldspar grains were also present. In general, the clays contained palygorskite with chlorite, kaolinite, and smectite admixture. Smectite predominated in certain concretion nuclei and formed authigenic spheroidal precipitates (Fig. 4c-e). Thus, the studied nuclei are represented by pelagic palygorskite clays. These are specifically edaphogenic [3] in character; to different degrees enriched in ultrabasic tectoadaphogenic matter. The authigenic smectite here apparently was related to the disintegration and reworking of fragments of hydrothermal substances, similar to those described in the transform fracture zone at 37°N [16].

The effect of edaphogenic matter on sediment composition is demonstrated in the core of station 4324. The 273-cm core consists of uniform miopelagic clays with numerous rounded and angular concretions (Fig. 2) that probably had been reworked. The age of the surficial sediments (0-5 cm) could not be accurately determined. Apparently, they were deposited during the Upper Pleistocene and the Holocene. Mud samples, taken by dredges (stations 4324/1 and 4333) contained the following coccolith species: Emiliana hexleyi (Fig. 5a), Cyclococcolithus leptoporus (Murr., Blackm.) Kpt., Helicopontospaera kamptneri Hay, Mohl., Oolithothus antillarum (Cohen) Cohen, Umbellosphaera tenuis (Fig. 5b), U. irregularis Paasche, Ceratolithus cristatus Kpt., and others. In station 4324/1 they belong to the Emiliana hexleyi Acme faunizone of 0-0.07 million years and in station 4333 in the Emiliana huxleyi zone of 0-0.27 millions years [14].

The planktonic foram fauna of station 4324 is of Pleistocene age. Solution-resistant species predominate: Globorotalia tumida (Brady), G. inflata (d'Orbigny), G. truncatulinoi-des (d'Orbigny), Pulleniatina obliquiloculata (Parker and Jones), Globoquadrina dutertrei (d'Orbigny), Globigerinita humilis (Brady), G. ruber (d'Orbigny), Globigerina calida (Parker) Globorotalia menardii (d'Orbigny). The small quantity of planktonic forams, their small number in most horizons (less than 1-3), the strong dominance of species with solution-resistant tests, the occurrence of specimens with different degrees of preservation but belonging to the same species, the small number of fragments (in a number of horizons they are totally absent) and the presence of iron-enriched tests indicate a stable solution regime during the accumulation of the 273 cm-sediment sequence. The absence of carbonate tests of benthic forams also suggests the chemically aggressive nature of water in dissolving carbonate matter, and low sedimentation rates (c. 1.5 mm/ka).

The presence of very small Pleistocene planktonic foram tests of good preservation in a number of horizons and their absolute dominance is related to sediment transport from distant shallower seafloor areas. The composition of these forms indicated a steady but slight transport of carbonate tests (horizons 5-35, 60-80, 105-110, 125-130, 145-165, 185-210, 225-230, and 255-273 cm), along with matter of different genesis. The amount of this matter made burial of small tests and their preservation possible. Small foraminifer fragments were not present. This is how sediments of Facies N [11] formed during the Pleistocene at station 4324. Judging from the absence of the benthic calcareous forams and fragments and not noted by the above-cited workers, the facies was subjected to the most intensive solution processes.

Chemically, the miopelagic clays of station 4324 differ from similar sediments of the northern equatorial Pacific zone (Table 2) by increased Ti and Al and lower Mn, Ca, and

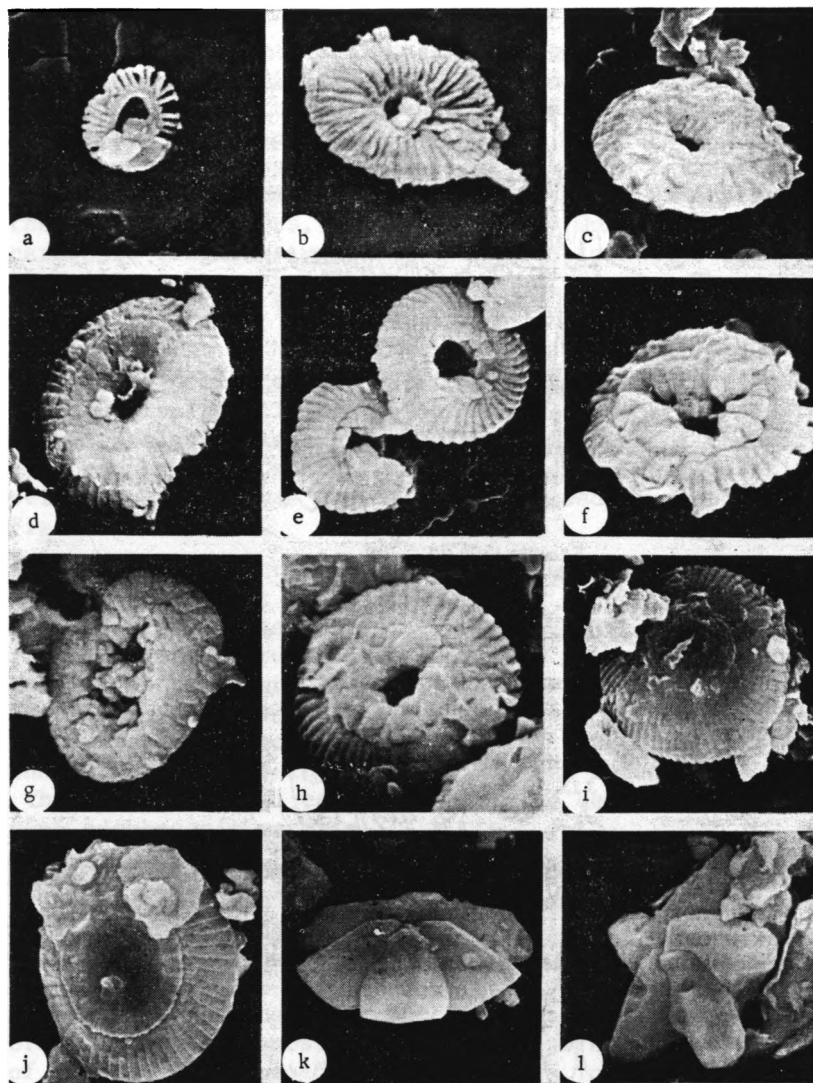


Fig. 5. SEM images of calcareous nannoplankton species. a) Emiliania huxley (Lohm.), Hay, Mohl., magnification 5000 $\times$; b) Umbellosphaera tenuis (Kpt.) Paasche, magnification 5000 $\times$; c) Coccolithus cavus Hay, Mohl., magnification 4000 $\times$; d) Coccolithus eopelagicus (Bram., Ried.) Kpt., magnification 2000 $\times$; e) Cyclicargolithus floridanus (Roth, Hay) Bukry, magnification 4000 $\times$; f) Coccolithus marismontium Black, magnification 5000 $\times$; g) Helicopontosphaera intermedia (Mart.) Hay, Mohl., magnification 3500 $\times$; h) Reticulofenestra cf. abisecta (Müll.) Roth, Thierst, magnification 5000 $\times$; i) Reticulofenestra bisecta (Hay, Mohl. Wade) Roth, magnification 2500 $\times$; j) Cribrrocentrum reticulatum (Gart.) Perch-Niels., magnification 3000 $\times$; k) Discoaster adamanteus Bram., Wilc., magnification 2500 $\times$; l) Discoaster aster Bram, Ried., magnification 3000 $\times$.

organic carbon concentrations. The generally variable MgO (2.0-7.1%) concentration increases from the core bottom to 5.4-7.1%, reflecting probably the admixture of edaphogenic ultrabasic rock matter. The sediments had a pelitic texture; increased sand and silt content occurs in the clay horizon with concretions. However, the heavy mineral distribution in these fractions is more complex (Table 2). Clayey sediments and rocks of the previously described ophiolitic rock association occur in concretion nuclei. Comparison of the distribution of concretion nuclei of various composition indicated (Table 3) that the number of sediment-bearing nuclei increased downward; i.e., stages can be distinguished in the supply of core matter. Massive concretion reworking, due to intensive tectonic movements during the

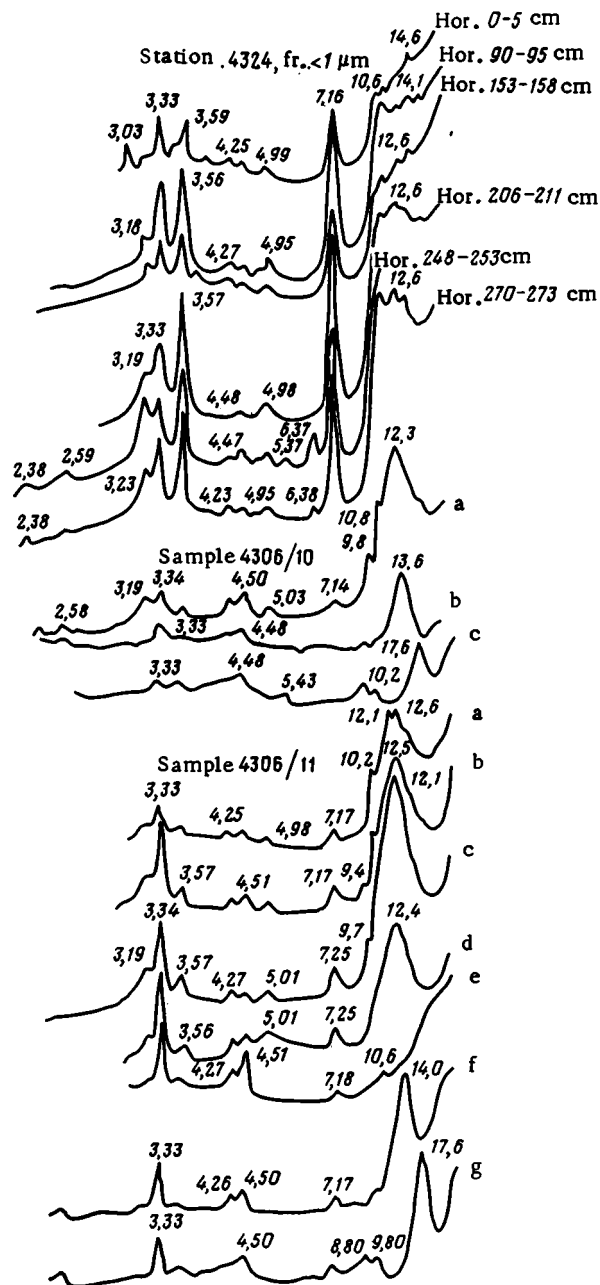


Fig. 6. Diffraction patterns of sediments and altered rocks. Sample 4306/10: a) air-dry; b) Mg-saturated; c) same, glycerine-saturated; sample #4306/11: a) foraminifer center; b) limestone without foraminifer center; c) total limestone; d) glycerine-saturated; e) HCl-treated; f) Mg-saturated; g) same, glycerine-saturated.

Pleistocene occurred on 4-5 occasions and individual concretions were repeatedly redeposited due to gravitational mass movements on slopes.

The relationship of minerals in coarse silty (0.1-0.05 mm) sediment fractions has been established after recalculating results of immersion analyses to nonbiogenic transparent (Table 4). Among the heavy minerals of station 4324, edaphogenic tremolite and actinolite predominated (Table 4f), along with monoclinic and rhombohedral pyroxenes, hornblende, olivine, chlorite, sphene, rutile, and prehnite. Minor amounts of terrigenous minerals were also present (garnets, epidote group minerals, corundum, apatite, zircon, and tourmaline)

and authigenic barite. The light minerals were dominated by terrigenous quartz, feldspars, acidic volcanic glass from land sources, authigenic zeolites, and glauconite. Edaphogenic serpentine (Fig. 4h) and basic plagioclase mineral occurred often; sometimes significant quantities. Judging from the uneven distribution of the most abundant tremolite and actinolite in the section, the supply of tectoadaphogenic matter to the sediments occurred repeatedly. The start of each cycle of redeposition was marked by increased concentrations of these minerals, while the end of the cycle was indicated by their lower concentrations. A similar, although depleted mineral complex also occurs in other Canary Basin stations (Table 4). In addition to the cited components, the coarse silty sediment fractions exhibited biogenic siliceous and carbonate fragments, grains of unknown identity, black ore minerals, Fe-hydroxides, individual pyrite spheres and Fe-Mn microconcretions. The microconcretions at station 4324 represented 42% of the 0.1-0.05 mm fraction and occurred very unevenly in the section.

The <0.001-mm fraction is dominated by chlorite, with significant admixtures of palygorskite (Fig. 4g), montmorillonite, illites, quartz, and feldspars. Apparently kaolinite and serpentine (Fig. 6) were also present. The large quantities of chlorite and palygorskite were derived from local (edaphogenic) sources. The increase of palygorskite concentration in the <0.001-mm fraction apparently was due to the increased Mg-content in sediments of station 4324 (Table 2, Fig. 6).

Thus, the fraction-by-fraction study of tectoadaphogenic matter in sediments of the Canary Basin sediments have shown that their mobilization essentially was due to cataclastic processes in deep-seated seafloor rocks in fracture zones. Near the source of edaphogenic matter from coarse clastics (gravel, rubble) was combined with sandy-silt and pelitic rock disintegration products in the sediments. Large fragments usually became concretion nuclei. With increasing distance from fault zones, the heterogeneity of concretion nucleus matter should apparently decrease but an effective method in the development of edaphogenic admixtures would be the mineral analysis of the coarse silty and subcolloidal sediment fractions. In certain instances the total chemical composition of the deposits appears to be the best criterion in identifying edaphogenic material.

Bioedaphogenic Matter. Bioedaphogenic (redeposited biogenic) sediments are quite typical of the NW Atlantic Ocean [13]. In our studied core samples they occurred on the east slope of the northern Mid Atlantic Ridge (station 4321; Fig. 2) and in the Guiana Basin (station 4306). In the core of station 4321 the bioedaphogenic deposits were represented by limey-clayey and limey (foram-bearing) Pleistocene turbidites, deposited in a miopelagic clay-setting. In station 4306 the bioedaphogenic carbonate (foram-dominated) sediment core of Pleistocene age formed through redeposition of Oligocene nannoplankton and planktonic forams. The source of the bioedaphogenic matter, as shown in the following, were Middle Oligocene clayey limestones, similar to those found in dredge samples at station 4306.

The Oligocene complex included the following nannoplankton species: Cyclicargolithus floridanus (Fig. 5e), Coccolithus eopelagicus (Fig. 5d), C. marimontium (Fig. 5f), Helicopontosphaera intermedia (Fig. 5g), Reticulofenestra bisecta (Fig. 5j), R. cf. abisecta (Fig. 5h), Discoaster aster (Fig. 5l), D. adamantus (Fig. 5k), and cribrocentrum reticulatum (Fig. 5j), etc. In addition to Oligocene taxa, quaternary species were also found in a cavity in the upper part of the limestones in the limey-clayey muds. These (Emiliana huxleyi and Syracosphaera pulchra). Burrows of burrowing organisms in the limey sediments were filled by limey-clayey muds of the Emiliana huxleyi Acme zone.

Planktonic forams indicated the similarly Oligocene age of clayey lime sediments at station 4306. In addition of typical Middle Oligocene taxa (Globigerina galavisi Bermudez, G. ciperoensis Bolli, Cassigerinella chipolensis (Cushman and Ponton), Chiloguembelina cubensis (Palmer), the Lower Oligocene Pseudohastigerina micra (Cole) and the Eocene Hantkenina alabamensis Cushman were also present. In the cavities and burrows rich finds of Pleistocene forams (shown in the following), mixed with Oligocene and Eocene species, were also made.

A complex of limey nannoplankton taxa, similar to that described in the clayey limes but richer, was found in the core of station 4306 that displayed foraminifer-bearing Pleistocene-Holocene sediments (0-1 cm) and Upper Oligocene (2-37 cm) deposits, separated by a thin ore crust. The Middle Oligocene complex included (in addition to species found in the limey deposits) Coccolithus cavus (Fig. 5c), and Sphenolithus predistentus Bram., Wilc. The last

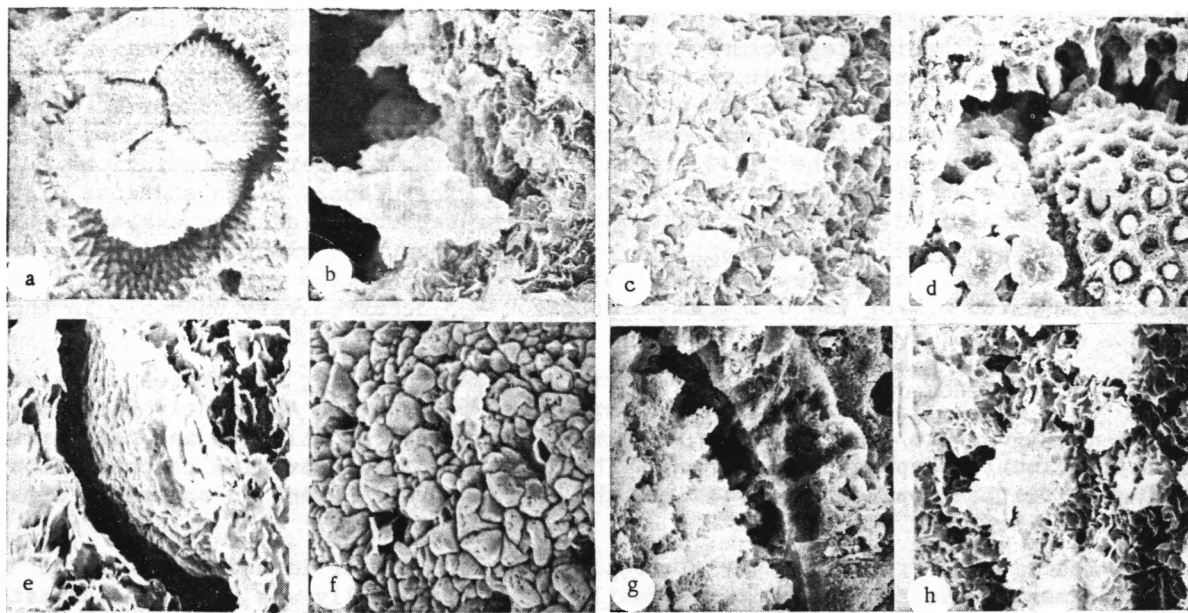


Fig. 7. Composition of altered rocks (SEM images): a) foraminifer test almost totally replaced by monomorphillonite, 125× magnification; b) same, calcitic relict of test, 1250× magnification; c) same, replaced test interior, 1500× magnification; d) peeled-off of newly formed core, after total replacement of foraminifer test by montmorillonite, 350× magnification; e) foraminifer test fragment, totally replaced by montmorillonite, 2000× magnification; f) etching marks on the exterior foraminifer test surface, 2250× magnification; g) fragment of slightly altered foraminifer test with interior, replaced by montmorillonite, 500× magnification; h) same, replaced interior, 1500× magnification.

species dates the 2-37 cm interval Middle Oligocene (NP 23 [17] or CP 17 [12]), corresponding to the 30-40 Ma [18] interval. Apparently the clayey limey deposits, despite absence of the index fossil, belong to this zone. Sediments of the 0-1 cm interval include species of the *Emiliania huxleyi* Acme Zone. Planktonic forams occurred throughout the core of station 4306. Their abundance (foram specimen number per 1 g sediment) ranged between 5200 (0-1 cm interval) and 45,300 specimens (34-35-cm interval). The specific composition varied greatly. Horizon 0-1 cm included *Glogigerinoides conglobatus*, *G. sacculifer* (Brady), *Globorotalia menardii*, *G. truncatulinoides*, *Orbulina universa* d'Orbigny, *Pulleniatina obliquilocatula*, and *Sphaeroidinella dehiscens* (Parker and Jones). These foram tests were gray, partly iron-enriched. The species composition in the fractions and the sediment as a whole indicate Pleistocene age. Sediment formed at the location where the core was taken. A small number of redeposited Oligocene species also occurred with the Pleistocene fauna: *Chiloguembelina cubensis*, *Globigerina ciperoensis* and others.

Lower in the section (2-37 cm) the number of planktonic foram specimens increased sharply; the frequency ranged between 10,200-45,300 specimens. Upper Middle and lower Upper Oligocene species included *Globigerina ciperoensis*, *G. angulituralis* Bolli, *G. angustum-bilicata* Bolli, and *G. galavisi*. The large quantity of *Chiloguembelina cubensis* and *Cassigerinella chipolensis* tests were somewhat unusual in the deposits. The Oligocene foram tests are pure white, large, well preserved. Tests, smaller than 0.25 mm were effected by solution. However, the tests of *C. cubensis* and *C. chipolensis* (smaller than 0.125 mm) did not exhibit traces of solution. Probably, they were transported from some distance.

In addition to Oligocene species with decreasing specimen number due to fewer smaller forms, the 19-20 and 36-37 cm interval included individual specimens of Pleistocene species. These were the most resistant to solution effects. They became enriched in iron and contained significant amounts of impurities. They included: *Globorotalia tumida*, *Pulleniatina obliquiloculata*, *G. truncatulinoides*, *G. menardii* and *G. dutertrei*. Comparison of faunas in these horizons and of the 0-1 cm interval indicates more intensive carbonate dissolution during the deposition of intervals 19-20, and 36-37 cm.

TABLE 4. Relationship of Nonbiogenic Transparent Minerals in Coarse-Silty Sediment Fractions, %

Sample number	Heavy minerals												Heavy minerals					Light minerals									
	garnets	hornblendes	tremolite and actinolite	monoclinic pyroxenes	orthorhombic pyroxenes	olivine	epidote group	biotite	corundum	chlorite	apatite	zircon	sphene	rutile	tourmaline	disthene	barite	staurolite	prehnite	serpentine	glauconite	quartz	Ca-feldspars	acidic feldspars	intermediate and basic feldspars	zeolites	acidic glass
4306/2	—	—	—	37,5	—	—	25,0	—	—	37,5	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	100	—
4306/3	15,4	15,4	—	—	—	—	30,8	—	15,4	—	—	15,4	—	—	—	7,7	—	—	—	—	—	4,8	—	—	—	90,4	—
4306/4	—	26,9	—	—	3,8	—	15,3	—	—	—	—	23,1	3,8	—	—	—	—	3,8	—	—	—	—	—	—	5,5	16,7	
4306/5	16,7	16,7	—	—	—	—	—	—	—	—	—	33,3	—	—	—	—	—	—	—	—	—	—	—	—	—	57,1	
4306-0-2	—	—	—	21,4	—	—	14,3	7,1	—	14,3	—	21,4	7,1	7,1	—	—	—	—	—	—	—	—	—	—	—	35,3	
4306-5-10	3,4	—	—	6,9	3,4	—	31,0	—	—	10,3	13,8	20,7	—	—	—	—	10,3	—	—	—	4,6	—	—	—	—	13,6	
4306-20-25	16,7	12,5	4,2	10,4	8,3	—	14,6	—	4,2	—	4,2	12,5	8,3	—	—	2,1	2,1	—	—	—	5,9	—	—	—	—	94,1	
4306-32-37	33,3	66,7	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	
4323-0-2	2,9	48,6	11,4	—	—	—	8,6	—	—	11,4	5,7	—	—	2,9	—	—	8,6	—	—	—	—	25,0	13,6	2,3	2,3	56,8	
4323-7-12	3,5	32,6	12,8	17,4	—	—	27,9	—	—	—	3,5	—	2,3	—	—	—	—	—	—	9,8	—	63,4	4,9	7,3	—	14,6	
4324/1-0-2	—	22,2	22,2	11,1	—	—	33,4	—	—	—	—	—	—	—	—	—	—	—	—	—	16,7	50,0	—	—	—	33,3	
4324/1-3-5	—	—	—	60,0	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—	100	—	
4324-0-5	6,7	26,6	26,7	—	—	6,7	—	—	—	—	—	—	13,3	—	—	—	—	—	—	—	—	—	—	—	—	—	
4324-15-19	9,4	—	18,8	15,6	—	—	9,4	—	—	6,2	6,2	—	12,5	—	—	—	15,6	—	—	1,3	0,9	—	60,0	—	—	—	
4324-40-45	1,4	11,6	65,2	8,7	1,4	—	4,3	—	—	—	—	1,4	5,8	—	—	—	—	—	31,6	—	—	77,6	8,9	4,3	—	3,0	
4324-90-95	—	13,8	55,2	3,4	—	1,7	13,8	—	—	—	3,4	5,2	—	—	—	—	3,4	—	—	—	—	47,4	15,7	5,3	—	—	
4324-110-115	5,6	27,8	13,9	5,5	—	—	25,0	—	—	—	8,3	13,9	—	—	—	—	—	—	—	—	—	90,4	4,8	—	—	—	
4324-120-125	—	11,4	60,0	14,3	2,9	—	8,6	—	—	—	—	—	2,9	—	—	—	—	—	—	—	100	—	—	—	—	—	
4324-135-140	3,0	22,4	40,3	17,9	—	—	13,4	—	—	—	3,0	1,5	1,5	—	—	—	—	—	—	—	—	66,6	16,7	16,7	—	—	
4324-140-145	2,7	21,6	67,6	2,7	—	5,4	—	—	—	—	5,4	—	—	—	—	—	—	—	—	—	—	81,8	9,1	—	—	—	
4324-147-152	1,6	22,2	22,2	20,6	7,9	1,6	4,8	—	—	4,8	1,6	—	9,5	1,6	—	—	3,2	—	—	15,0	—	30,0	—	10,0	5,0	40,0	
4324-153-158	—	49,1	30,9	—	—	0,9	15,4	—	—	—	1,8	0,9	—	—	0,9	—	—	—	—	—	100	—	—	—	—	—	
4324-160-165	—	10,7	39,3	5,4	5,3	—	1,8	—	—	21,4	3,6	—	10,7	1,8	—	—	—	—	—	10,7	—	60,7	—	7,1	3,6	17,9	
4324-177-182	—	25,0	33,3	17,8	—	6,0	8,3	—	—	—	1,2	—	—	—	—	—	8,3	—	—	—	—	60,0	—	25,0	—	15,0	
4324-196-201	1,8	32,1	37,5	12,5	1,8	—	8,9	—	—	—	—	1,8	3,6	—	—	—	—	—	—	17,6	—	41,2	17,6	5,9	5,9	11,8	
4324-201-206	1,1	5,3	73,7	4,2	—	—	5,3	—	1,1	1,1	2,1	2,1	2,1	—	1,1	—	1,1	—	—	22,2	—	72,2	5,6	—	—	—	
4324-206-211	—	2,2	79,5	1,1	—	—	4,5	—	—	—	—	1,1	11,4	—	—	—	—	—	—	9,1	—	68,2	18,2	4,5	—	—	
4324-230-235	1,6	21,0	29,8	—	—	1,6	9,7	—	—	—	—	—	7,2	—	—	29,0	—	—	—	—	—	70,6	9,8	4,9	4,9	9,8	
4324-248-253	—	20,5	69,2	—	—	—	—	—	—	—	—	1,3	2,6	—	—	—	—	—	6,4	87,5	—	—	—	—	—	12,5	
4324-263-268	0,8	12,5	65,8	5,0	1,7	—	—	—	—	1,7	—	—	11,7	—	—	—	—	—	—	45,5	—	26,7	20,0	6,6	—	—	
4324-270-273	—	8,2	87,3	—	—	—	1,8	—	—	—	—	—	0,9	—	—	—	—	—	—	—	—	78,7	—	7,1	—	7,1	
4333-0-3	5,7	54,3	5,7	17,1	—	—	17,1	—	—	—	—	—	—	—	—	—	—	—	—	—	22,2	33,4	11,1	—	—	33,3	

TABLE 5. Chemical Composition of Altered Rocks

Sample No.	Si	Al	Fe	Mn	Ti	Sr	Ca carb	Mg carb	Mg tot	Mo	Cu	Zn	Ni	Cr	Li	Pb	Co	V	Cd
	%										$n \cdot 10^{-4} \%$								
4306/10	21,8	2,45	16,0	0,245	0,09	0,071	0,57	0,84	1,47	<0,003	75	120	200	17	29	60	36	310	18
4306/11	24,1	6,05	12,0	0,120	0,21	0,009	0,90	0,61	1,82	<0,003	38	110	130	34	46	80	29	140	8

The distribution characteristic of Oligocene and Pleistocene planktonic foraminifers in the core of station 4306 clearly shows that the Oligocene sediments underwent redeposition and this also occurred twice in the Pleistocene Globorotalia truncatulinoides zone. The start of the redeposition is fixed by the presence of Pleistocene forms in the 0-1, 19-20, and 36-37 cm intervals. These intervals exhibited the lowest foram counts. Sediment was transport, probably as the result of submarine landslides, from seafloor areas of c. 2000 m depths. In the area of the Bermuda Rise, at the shores of Cuba, in the Puerto Rico Trench such slides redeposited Oligocene fauna into Late Pleistocene sediments [13]. Thus, a complex micropaleontological characterization of the studied cores define sediments in core of station 4306 (2-37-cm interval) as bioedaphogenic Pleistocene deposits, while the clayey-limey deposits are considered Middle Oligocene bedrock outcrops.

Based on chemical and granulometric (Table 4) parameters, the Middle Oligocene coccolithic-foraminifer-dominated limey sediments (samples 4306/3, 4) are very similar to bioedaphogenic foraminifer-dominated sediments (station 4306, 5-37-cm interval). However, the latter ones were significantly enriched in CaCO_3 and to a lesser extent in Fe, Si, Al, Mg, and K. They contain smaller amounts of the pelitic fractions. This resulted due to limey sediment removal: the coarse-grained fractions (foraminifer tests and detrital mineral grains) were redeposited close to their origination, while the fine fractions (coccoliths and clay minerals) were carried generally farther.

Hydrothermally Altered Edaphogenic Matter. In addition to bioedaphogenic sediments hydrothermally altered edaphogenic matter, including nuclei of rounded and angular concretions were also present at station 4306. In ellipsoidal concretions (Table 1; sample 4306/9) the clay matter of the cores was intensively saturated by goethite. Nuclei of angular concretions were formed by brownish-green and yellowish brown rocks. Samples of the 4306/10 category (altered argillite) consist of fine flaky clay aggregate, including 7-10% planktonic foraminifer content. The periphery of the nucleus was highly iron-enriched. The foraminifer tests occasionally were totally dissolved; more often replaced yellowish-brown clay aggregate or Fe hydroxides. Unaltered tests were found only in small cavities and apparently were introduced at later times.

In samples of the 4306/11 category (altered clayey limey deposit) the clayey substrate originally included 40-45% planktonic foraminifer tests (limey-clayey deposit). Presently almost all the tests are dissolved (small limestone fragments also occurred) and were replaced by brownish-green fine-flaky clay aggregate. The interior of the foram tests were dark green (Fig. 7a-e). Typical Pliocene species (Globorotalia margaritae Zone [19]) occurred among the tests that were replaced: G. margaritae Bolli and Bermudez, G. humerosa Takayanagi and Saito, Globigerina nepenthes Todd, Orbulina suturalis Brönnimann, and Sphaeroidinellopsis paenedehiscens Blow. The test replacement thus did not occur prior to the Middle Pliocene.

The concretion nuclei of the studied samples were characterized by high Fe-concentrations (12-16%) and low Ca and Mg content (Table 5).

Authigenic Fe-bearing montmorillonite (Fig. 6) was the dominant sediment component. A mixture of illite, chlorite, kaolinite, quartz and feldspars also occurred. A similar alteration of carbonate matter also occurred immediately under the ore crust in the Middle Oligocene limey deposits (Fig. 7f-h) but such changes were minor in Pleistocene foraminifer-bearing deposits at station 4306. Only the redeposited foraminifers had been altered in those sediments.

Judging by the composition of the altered sediments and the replacement characteristics of the original components, we may assume that deposits of various ages had been affected by hydrothermal processes during Pliocene and the Pleistocene within active fault zones that extended westward of the Vema Transform Fault Zone (Fig. 1). Subsequent erosional and gravitational processes during the Pleistocene led to fragmentation of the altered matter and to formation of bioedaphogenic sediments.

The data presented indicate the great advantages of complex studies of concretion nuclei and the enclosing sediments. In particular, the composition of tectoedaphogenic substances indicated that the transform Kane Fracture Zone extends further toward the ESE than assumed earlier on the basis of seismic data [20]. Indications of hydrothermal activity have also been documented at the western end of the transform Vema Fracture Zone (Guiana Basin).

The studied regions are tectonically active. Tectosedaphogenic and biosedaphogenic sediments are being deposited here. Approximately five episodes of tectonic activity have been recorded in the Pleistocene deposits of the Canary Basin (Fig. 2; Table 3). However, based on the coarse silt fraction of sediments and the distribution pattern of planktonic forams, the number of tectonic events had been much greater. During the Late Pliocene and Pleistocene tectonic activity in the fracture zones of the Guiana Basin led to the uncovering of Oligocene limestones and hydrothermal alteration of sediments. The same activity formed biosedaphogenic sediments during the Pleistocene, probable time-correlatives of Late Pleistocene biogenic turbidites of the Bermuda Rise, the Puerto Rico Trench, and nearshore areas of Cuba [13].

Cataclastic alteration of rocks on the seafloor mobilized primarily the tectosedaphogenic matter. With increasing distances from its sources, the number of concretion nuclei, composed of igneous and metamorphic rocks gradually decreases, while the percentage of sedimentary and biogenic nuclei (bone fragments, teeth) increases. The effects of edaphogenic components, derived from greater distances, may be evaluated on the basis of sandy-silty and pelitic sediment component values.

LITERATURE CITED

1. I. O. Murdmaa, "Oceanic facies," in: *Oceanology and Geology of Oceans; Sediment Deposition and Oceanic Magmatism* [in Russian], Nauka, Moscow (1979), pp. 269-306.
2. I. O. Murdmaa and T. V. Rozanova, "Edaphogenic minerals," in: *Oceanology and Geology of Oceans. Sediment Deposition and Oceanic Magmatism* [in Russian], Nauka, Moscow (1979), pp. 210-214.
3. V. P. Petelin, "Mineral formation in deep water sediments," in: *History of the World Ocean* [in Russian], Nauka, Moscow (1971), pp. 207-219.
4. T. V. Rozanova, "Sediments in Rift Zones of the central Indian Ocean ridges," in: *History of the World Ocean*, Nauka, Moscow (1971), pp. 174-194.
5. V. N. Sval'nov, "Recent mineral provinces of the eastern Indian Ocean," in: *Complex Studies of the World Ocean* [in Russian], VINITI (1975), pp. 220-224.
6. V. N. Sval'nov, *Quaternary Sedimentation in the East Indian Ocean* [in Russian], Nauka, Moscow (1983).
7. V. N. Sval'nov and V. V. Gordeev, "Chemical composition of sediments," in: *Fe-Mn Concretions of the Central Pacific Ocean* [in Russian], Nauka, Moscow (1986), pp. 68-88.
8. A. V. Soldatov and G. S. Kharin, "Mineral composition of deep water deposits in the Atlantic Ocean," in: *Ocean Studies* [in Russian], Izd. Akad. Nauk SSSR, No. 26, Moscow (1979), pp. 6-48.
9. A. V. Soldatov, G. S. Kharin, and E. M. Emel'yanov, "Recent terrigenous mineral provinces in the Atlantic Ocean," *Litol. Polezn. Iskop.*, No. 6, 67-79 (1976).
10. T. Yu. Uspenskaya, A. I. Gorshkov, and A. V. Sivtsov, "Internal structure and mineralogical composition of depositional oceanic concretions," *Izv. Akad. Nauk SSSR, Ser. Geol.*, No. 5, 25-37 (1987).
11. W. H. Berger and U. von Rad, "Cretaceous and Cenozoic sediments from the Atlantic Ocean," *Initial Reports of DSDP*, U.S. Government Printing Office, Washington, 14, 787-886 (1972).
12. D. Bukry, "Biostratigraphy of Cenozoic marine sediments by calcareous nonnofossils," *Micropaleontology*, 24, No. 1, 44-60 (1978).
13. D. B. Ericson, M. Ewing, G. Wollin, and B. C. Heezen, "Atlantic deep-sea sediment cores," *Bull. Geol. Soc. Am.*, 72, 193-286 (1961).
14. S. Gartner, "Calcareous nannofossil biostratigraphy and revised zonation of the Pleistocene," *Marine Micropaleontology*, No. 2, 1-25 (1977).
15. P. Halbach, R. Giovanoli, and D. von Borstel, "Geochemical processes controlling the relationship between Co, Mn and Fe in early diagenetic deep-sea modules," *Earth Planetary Sci. Lett.*, 60, 226-236 (1982).
16. M. Hoffert, A. Perseil, R. Hekinian, et al., "Hydrothermal deposits sampled by diving saucer in Transform Fault A near 37°N on the Mid-Atlantic Ridge, FAMOUS Area," *Oceanologica Acta*, 1, No. 1, 73-86 (1978).
17. E. Martini and T. Worsley, "Standard Paleogene calcareous nanoplankton zonation," *Nature*, 225, 560-561 (1970).
18. H. Okada and D. Bukry, "Supplementary modification and introduction of code numbers to the low latitude coccolith biostratigraphic zonation (Bukry, 1973, 1974)," *Marine Micropaleontology*, No. 4, 321-325 (1980).

19. R. M. Stainforth, J. L. Lamb, J. H. Beard, et al., "Cenozoic planktonic foraminiferal zonation and characteristics of index forms," Univ. Kansas Paleontol. Inst., Harold Normal Fisk Mem. Paper, Lawrence, Kansas, USA (1975).
20. L. R. Sykes, "Mechanism of earthquakes and nature of faulting on the midoceanic ridges," J. Geophys. Res., 72, No. 8, 2131-2144 (1967).

GEOCHEMICAL CRITERIA FOR CORRELATION OF SILICEOUS STRATA AND PALEOGEOGRAPHICAL RECONSTRUCTIONS

Yu. G. Volokhin

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In the article, we discuss the content of rock-forming elements and twelve rare elements, their ratios (moduli), and correlations within lithological types of silicites identified in the composition of the mineral mixture in the geosynclinal deposits of the Triassic-Jurassic Sikhote-Alin and Cambrian-Lower Carboniferous deposits of the Mongolian-Okhotsk region. The typomorphic features associated with the lithological types of silicites, and dependences of their chemical compositions and parageneses of chemical elements upon paleogeographic criteria for stratigraphic correlation of siliceous strata and paleogeographic reconstructions.

The use of geochemical data for stratigraphic correlations of siliceous strata is based upon the discovery of similarities between the chemical characteristics and associations of chemical elements in rocks of comparable sections [10, 19]. Reconstructions of physico-geographical depositional environments of silicites with the aid of geochemical indicators [36-38] are based upon present-day suppositions. The patterns of decreasing concentrations of Al and Ti and increasing concentrations of Fe and Mn in the Quaternary sediments of the Pacific Ocean as one proceeds from the shore zone to the pelagic zone and further out to the exhalation-hydrothermal metalliferous muds of the Eastern-Pacific rises [30] allow us to use Ti/Al , $Al/(Al + Fe + Mn)$, $(Fe+Mn)/Ti$ and other quantities to estimate the contributions of the terrigenous material and the material of the oceanic crust (hydrothermal, basaltic detritus) to the sedimentary process [21, 31].

The contents of Fe, Mn, and Al in the skeletons of planktonic organisms are insignificant [35], and, in siliceous muds, they are determined by the quantity and composition of the admixture. M. Steinberg and M. S. Mpodozi [37] classified radiolarites on the basis of a manganese anomaly expressed by the difference in the contents of Mn and Fe normalized to basalts ($Mn_F/Mn_B - Fe_F/Fe_B$) and on the basis of the $Al/(Al + Fe + Mn)$ modulus. They classified radiolarites into: 1) radiolarites subjected to a strong influence from oceanic crust (impoverished of Al and enriched in Fe and Mn); 2) pelagic radiolarites; and 3) radiolarites contaminated with clastic silic material (enriched in Al and impoverished of Fe and Mn). They also proposed subclassifying silicites according to the positions of straight-line regressions for the dependence of Fe upon Al. It is believed that the lower the value of $Al/(Al + Fe + Mn)$ or the greater the slope of the straight-line regression for Fe vs Al, the greater the distance from the source of the terrigenous material and the more pelagic the environment where the silicites were deposited [33, 36-38]. The possibility of using Fe and Al ratios to identify different sedimentary environments of bedded cherts, despite insufficient statistical significance associated with the ratios, was pointed out in a report on the Jurassic silicites of the Pindos zone in Greece [29].

Applying present-day interpretation of geochemical data to geosynclinal silicites could be questionable because of the dissimilar compositions, textures, and parageneses with other

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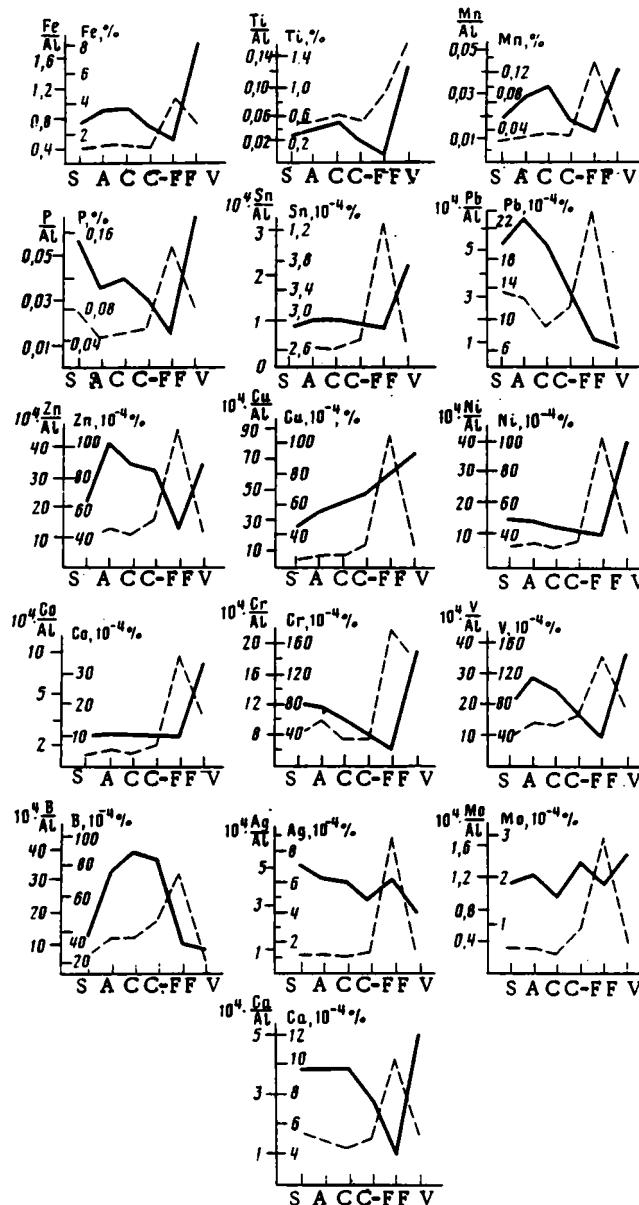


Fig. 1. Average contents of elements and their ratios to Al in the Triassic-Jurassic rocks of Sikhote-Alin. Rocks: S) Sandstones; A) aleuroeites; B) argillites; C-F) clayey chert; F) chert; V) subsilicic volcanites (content of elements: solid line; ratio of elements to aluminum: dotted line).

rocks, because of differences between the depositional environments of modern siliceous muds and the silicites of folded regions, and because of the problematical nature of the origin of the latter [23, 25, 34]. The investigations [36-38] just referred to were not based upon any particular petrographic classification and, therefore, did not take into consideration possible specific geochemical differences between lithological types of silicites.

In the present article, we present patterns of distribution associated with rock-forming elements and 12 rare elements in the early Mesozoic silicites of Sikhote Alin and in the Cambrian-Lower Carboniferous silicites of the Mongolian-Okhotsk region. We also evaluate the applicability of geochemical criteria to the correlation of siliceous strata and to paleogeographic reconstructions. The sections studied, the detailed petrographic and geochemical characteristics of the silicites and the enclosing rocks, and the analytical method are satisfactorily reviewed in [7, 8]. New stratigraphic data recently obtained [3, 14] allow us to refine the age estimate for the early Mesozoic siliceous formation of the Sikhote Alin;

TABLE 1. Order of Concentrations of Elements within Admixtures in Silicites

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16
I. $K = \text{El}/\text{Al}_{\text{silic}} : \text{El}/\text{Al}_{\text{sand}}$ Sikhote-Alin Jaspers															
Ga, Pb 2,6	P 3	Ti 3,1	Cr 3,5	V 4,8	B 6	Fe 6,3	Ag 6,4	Mo 7	Zn 7,1	Mn 7,3	Sn 8,3	Ni 11	Co 14	Cu 24	
Cherts															
Ti 1,8	Pb 2,1	P 2,2	Ga 2,4	Cr 3	V 3,9	Fe 4,6	Zn 4,8	Mn 5	Mo 5,6	B 5,8	Sn 6,8	Ni 7,2	Ag 7,6	Co 8,7	Cu 20
Phtanites															
Ti 1,6	Zn 1,7	Mn 2	P 2,7	Fe 3	Co 3,5	Pb 4,4	Ni 5	Cr 5,2	Ga 5,5	Sn 6,8	B 11	Cu 20	V 25	Ag 105	Mo 130
Mongolian-Okhotsk region Jaspers															
Ti 0,2	Pb 1,0	Cr 1,1	Ga 1,2	V 1,5	Fe 1,8	Ag 2,3	Sn 2,4	P 2,9	Ni 3,1	B 3,2	Mo 3,3	Zn 3,4	Co 3,6	Cu 4	Mn 4,1
Cherts															
Ti 0,7	Pb 2	Cr 2,5	Fe 2,6	Ga 2,7	Mn 3,2	V 3,4	P 3,8	Ni 3,9	Ag 4	Sn 4,8	Co 4,9	Zn 5	Mo 5,2	B 5,7	Cu 11
Phtanites															
Ti 0,3	Ga 2,3	Fe 2,6	Co, Mn 2,8	B 3	Cr 3,1	Pb 3,3	Sn, P 5,8		Zn 8	Ni 8,3	Cu 14	V 30	Mo 100	Ag 138	
II. $K_1 = \text{El}/\text{Al}_{\text{jasp}} : \text{El}/\text{Al}_{\text{chert}}$ Sikhote-Alin															
Ag 0,8	B 1	Ga 1,1	Cr 1,17	Cu, Sn 1,2	Pb, V 1,23	Mo 1,25	P, Fe 1,36	Mn 1,46	Zn 1,48	Ni 1,5	Co 1,6	Ti 1,7			
Mongolian-Okhotsk region															
Ti 0,3	Cr 0,4	Ga, V 0,44	Pb 0,49	Sn 0,5	Cu, B 0,56	Ag 0,58	Mo 0,6	Zn 0,68	Fe 0,69	Co 0,7	P 0,76	Ni 0,8	Mn 1,3		

we now consider it to be Middle Triassic to Lower Jurassic rather than Upper Triassic to Lower Jurassic.

Geochemical Differences between Lithological Types of Silicites

Investigations of the siliceous rocks in folded regions clarified the typomorphic geochemical features associated with several types of silicites: enrichment of phtanites with Mo, V, Ag, Fe, and several other elements [1, 24, 26, 28, 32] and enrichment of jaspers with Fe, Mn, and sometimes other elements [4, 23]. Meanwhile, the very process of identifying types of silicites remains ambiguous and the majority of geologists make identifications on the basis of a combination of morphological criteria. This has led to contradictory understandings of even such entrenched terms as "jasper" and "phtanite." A classification of silicites according to dispersed mineral admixtures [8] is used in the present article: iron oxides and ferric hydrates (jaspers), iron sulfides and carbonates (cherts), and organic carbonaceous material (phtanites). Rocks with SiO_2 contents (free) greater than 80% are classified as silicites proper, and rocks with SiO_2 contents of 50-80% are classified as clayey silicites.

In the rocks of the terrigenous-siliceous series located within Sikhote Alin, the concentrations of the majority of other elements decrease with increasing SiO_2 content, reaching minimal values in the most highly siliceous silicites. At the same time, the ratio of concentrations of rock-forming and trace elements to aluminum increases, reflecting increases in concentrations of these elements in the impurities within the silicites (Fig. 1). A situation analogous to that presented in Fig. 1 can be seen in the sedimentary rocks of the Paleozoic geosynclinal complex in the Mongolian-Okhotsk folded region [8]. The degree to which admixtures in the silicites are enriched with one or another element can be determined by comparing ratios of average contents of elements to Al in siliceous rocks and sandstones,

TABLE 2. Average Chemical Compositions of Lithological Types of Silicites in Sikhote-Alin

Oxides, %; trace elements, 10 ⁻⁴ %	Silicite			Clay silicites		
	jaspers (26/38)	cherts (92/165)	phthanites (23/27)	clayey jaspers (8/10)	clayey cherts (53/72)	clayey phthanites (33/37)
SiO ₂	91.50	93.96	91.84	79.69	79.16	80.55
TiO ₂	0.22	0.13	0.13	0.58	0.43	0.39
Al ₂ O ₃	1.64	1.76	2.35	7.24	9.46	7.39
Fe ₂ O ₃	1.79	0.43	0.66	2.98	1.19	1.36
FeO	1.20	1.61	1.28	1.30	2.01	0.99
MgO	0.34	0.39	0.29	1.22	1.20	0.96
CaO	1.17	0.32	0.14	1.37	0.61	0.22
MnO	0.08	0.05	0.03	0.14	0.07	0.04
K ₂ O	0.36	0.41	0.67	1.54	1.97	1.73
Na ₂ O	0.30	0.16	0.09	1.39	0.84	0.12
P ₂ O ₅	0.15	0.11	0.13	0.13	0.17	0.22
Calcination loss	1.15	0.50	2.11	2.39	2.51	5.66
C _{org}	0.05	0.11	1.13	0.06	0.11	2.06
C _{carb}	0.12	0.02	0.00	0.11	0.03	0.00
Sn	3.5	2.8	3.4	3.5	3.0	3.7
Pb	6.8	7.3	21	15	14.7	24
Zn	57	50	77	130	95	78
Cu	90	75	97	82	68	82
Ni	54	38	39	61	42	33
Co	13	9.1	8.0	15	11	3.9
Cr	23	20	44	44	42	59
V	36	31	234	77	89	324
B	28	24	57	41	82	120
Ag	0.05	0.09	1.15	0.04	0.07	1.09
Mo	1.8	1.6	33	1.5	2.4	54
Ga	3.7	3.0	9.7	7	8	14.5
SiO ₂ (free)	87.6	89.7	86.2	62.3	56.5	62.8
ΣFe	2.18	1.55	1.46	3.12	2.39	1.72
Al/(Al + Fe + Mn)	0.28	0.37	0.46	0.54	0.67	0.69
K ₂ O/Na ₂ O	1.20	2.56	7.4	1.11	2.35	14.4
Fe ²⁺ /ΣFe	0.43	0.81	0.68	0.32	0.65	0.45
Mn/Fe	0.028	0.027	0.016	0.035	0.023	0.018

Explanation. In this and the following tables, the rock-forming oxides were determined chemically; the trace elements were determined by a quantitative spectral method at the Far-East Geological Institute. The number of samples is given in brackets (in the numerator: for rock-forming oxides; in the denominator: for trace elements).

the last and first members in a differentiated series of geosynclinal sedimentary rocks. The elements can be placed in a definite sequence in order of increasing values for the coefficient $K = \text{El}/\text{Al}_{\text{silic}}/\text{El}/\text{Al}_{\text{sand}}$ (Table 1).

In each of the regions discussed, the series of elements in the cherts and jaspers are similar in that Pb, Ga, Cr, V, Ti (also, P within Sikhote-Alin, but Fe within the Mongolian-Okhotsk region) are positioned at the beginning of each series, while Mo, Co, and Cu (Ni and Sn also in Sikhote-Alin, but Zn and B in the Mongolian-Okhotsk region) are positioned at the end of each series. These series are similar to the most common mobility series for elements under hypogene conditions, established both on the basis of removal of elements during weathering [12] and on the basis of the ratios of dissolved and suspended forms in river flow [6, 11, 13]. Among the groups under discussion, the mobilities of Ti, Ga, Pb, Cr, and V (sometimes Fe) are usually minimal, but the mobilities of Mn, Ni, Co, Mo, and Cu are usually maximal. The effects of diluting the amount of admixture with authigenic silica and concentrating elements within the admixture to degrees corresponding to their mobilities results in low contents of rock-forming elements (except for SiO₂) and low contents of poorly mobilized trace elements in cherts and jaspers in comparison with clayey cherts and clayey jaspers (Tables 2 and 3). The clay minerals in one of the actual sections are significantly (at a 5% level of reliability) enriched in the poorly mobilized elements Ti, Ga, Pb, Cr, V, and also Zn and B, relative to the silicites. The latter two elements are concentrated in the clayey, essentially hydromicaceous fraction (the total quantity of this fraction is higher in clay silicites. The more mobile elements, Zn, Ni, Mo, Ag, Co, and Cu are present in

TABLE 3. Average Chemical Compositions of Silicites in the Mongolian-Okhotsk Region

Oxides, %; trace elements, 10 ⁻⁴ %	Clay silicites	Cherts	Phanmites	Cherts S-D ₁		Cherts D ₂ -C ₁	
	Є ₁ - C ₁ (13/27)	Є ₁ - C ₁ (51/67)	S (10/13)	Galam River (4/5)	Tyl' River (26/31)	Galam River (9/6)	Feklistova Island (5/6)
SiO ₂	93,49	93,89	94,84	94,66	94,05	91,96	93,63
TiO ₂	0,04	0,05	0,01	0,08	0,01	0,02	0,15
Al ₂ O ₃	2,21	1,49	0,85	2,00	1,38	2,58	0,31
Fe ₂ O ₃	0,99	0,57	0,18	0,18	0,49	0,93	0,95
FeO	0,62	1,50	1,23	0,82	2,04	1,51	1,39
MgO	0,61	0,70	0,43	0,45	0,66	1,03	0,81
CaO	0,17	0,30	0,05	0,18	0,31	0,14	0,40
MnO	0,13	0,09	0,04	0,04	0,07	0,10	0,12
K ₂ O	0,54	0,47	0,13	0,70	0,36	0,94	0,54
Na ₂ O	0,22	0,22	0,07	0,06	0,20	0,23	0,34
P ₂ O ₅	0,15	0,13	0,08	0,13	0,15	0,15	0,06
Calcination loss	0,64	0,62	2,11	0,50	0,38	0,69	0,85
C _{org}	0,05	0,09	1,45	0,09	0,12	0,14	0,06
C _{carb}	0,00	0,04	0,00	0,00	0,02	0,01	0,05
Sn	2,5	3,9	3,1	2,8	5,2	2,8	3,0
Pb	7	11	13	6,8	13,6	12,3	11,2
Zn	42	43	53	25	42	48	69
Cu	79	149	121	43	237	112	136
Ni	38	38	64	18	45	29	62
Co	16	18	6,6	9	22	15	28
Cr	20	34	41	14	51	23	22
V	34	56	431	20	80	41	46
B	41	51	25	27	70	53	34
Ag	0,06	0,08	1,6	0,06	0,09	0,07	0,05
Mo	2,0	2,2	30	—	2,6	—	1,8
Ga	4,6	7,0	5,2	3,8	8,7	5,5	—
SiO ₂ (free)	88,2	90,3	92,8	89,9	90,7	85,8	92,9
ΣFe	1,17	1,56	1,08	0,76	1,90	1,81	1,73
Al/(Al + Fe + Mn)	0,48	0,33	0,29	0,57	0,27	0,42	0,08
K ₂ O/Na ₂ O	2,5	2,1	1,9	11,7	1,8	4,1	1,6
Fe ²⁺ /ΣFe	0,41	0,75	0,88	0,84	0,84	0,65	0,62
Mn/Fe	0,09	0,04	0,03	0,04	0,03	0,04	0,05

Note. Lines drawn through positions on this and the following tables indicate absence of data.

quantities similar to those in untypical clay silicites; sometimes, however, silicites from the same sections are even enriched by comparison [8].

In both regions, the jaspers can be distinguished from the cherts by lower content of C_{org} and higher content of Mn and also by larger portion of Fe³⁺ in the composition of the bulk iron (see Tables 2 and 3). These, and also the more cardinal differences in the parageneses of the chemical elements (see below) within the jaspers and cherts were mainly caused by the oxidizing conditions associated with the former and the reducing conditions associated with the latter. In the cherts of Sikhote-Alin, the average concentrations of Fe and the majority of the trace elements are less than in the jaspers; in the Mongolian-Okhotsk region, they are higher in the silicites and lower in the jaspers (see Tables 2 and 3). Within both regions, a general tendency toward maximum enrichment of admixtures in jaspers with Mn, Fe, Zn, Co, and Ni in comparison with admixtures in silicites has been noted on the basis of the ratio $K_1 = \text{El}/\text{Al}_{\text{jasp}}/\text{El}/\text{Al}_{\text{silic}}$ (see Table 1).

In contrast to the series for jaspers and cherts, Pb, Cr, Ga, B, V, Ag, and Mo are shifted to the right in the series for phanmites. These elements, and also Cu and Ni, are usually highly concentrated in bitumen silicites of various ages and locals [1, 24, 26, 28, 32] and also in bitumen limestones [40]. The phanmites and clayey phanmites of the Sikhote-Alin and Mongolian-Okhotsk regions are maximally enriched in V, Ag, and Mo up to concentrations exceeding those of the clark within clayey rocks: two- to threefold in the case of V, 20-50 fold in the cases of Mo and Ag. These elements are typomorphic for carbonaceous silicites. High concentrations of Cu, Ni, V, and Mo are common in oils and bitumens, except in the oils and bitumens found in the sapropelic muds of the Black Sea, where concentrations of the above named elements correlate positively with C_{org} [5]. Small concentrations Ni and Cu were discovered in live plankton (6.5 and 13% of the concentrations of the corresponding elements in

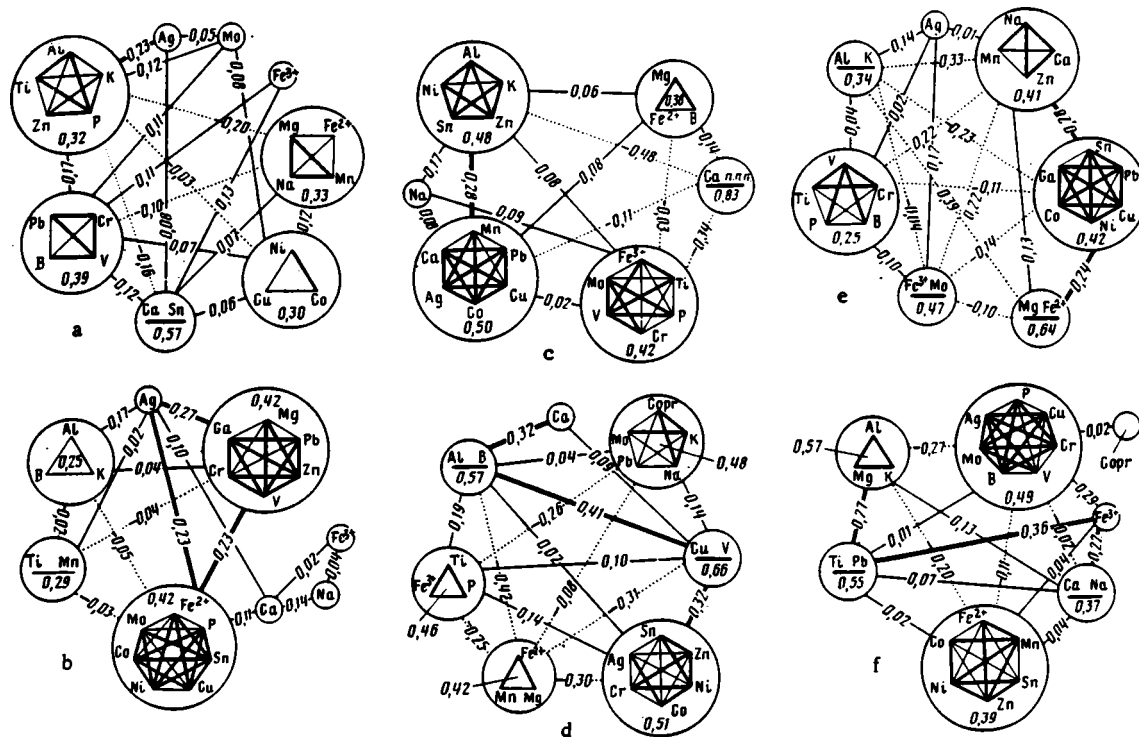


Fig. 2. Structural diagrams of correlations between chemical elements in Middle Triassic to Lower Jurassic silicites of Sikhote-Alin. a) cherts of Sikhote-Alin (37 samples); b) cherts of northern Sikhote-Alin (34 samples); c) jaspers (26 samples); d) phtanites (15 samples); e) clayey cherts (42 samples); f) clayey phtanites (24 samples). Thick lines identify links with correlations significant at the 95% confidence level.

the sapropel), but Mo and V were found to play almost no role. The accumulation of Mo and V in sapropelic muds was due to the sorption of these elements from sea and mud waters, along with the formation of metalloorganic complexes with fulvic acids [5]; the accumulation took place during the stages of sedimentation and diagenesis.

In the phtanites of Sikhote-Alin and the Mongolian-Okhotsk region, the isotopic compositions of the carbon lie within a narrow range of values, from 27 to 32.5% (identical to the isotopic composition of bitumens and some oils). This suggests a marine sapropelic origin for the organic matter in the phtanites [8]. The mechanism of accumulation of trace elements in the carbonaceous silicites is probably the same found for the sapropelic muds of the Black Sea and the sharp geochemical differences between the phtanites on the one hand and the jaspers and cherts on the other are due to the significant concentrations of organic matter within them.

Associations of Chemical Elements in Silicate Lithotypes

The most thoroughly investigated geochemical associations are those in the Middle Triassic to Lower Jurassic silicites of Sikhote-Alin [8]. The associations of elements were classified on the basis of a matrix of partial correlation coefficients, with SiO_2 eliminated by the method of forming compact groups [20]. Y. E. Yudovich [27] represented the correlations in the form of structural diagrams in which negative and zero correlations for unassociated elements were not shown.

Cherts (Fig. 2a, b). In the cherts in southern Sikhote-Alin (sections at Uborka settlement-Samarka settlement, Fig. 3), one can distinguish the following associations: Al-K-P-Zn-Ti, Pb-Cr-V-B, Ca-Sn, Mg- Fe^{3+} -Mn-Na, Ni-Co-Cu, and the unassociated elements Fe^{3+} , Mo, and Ag. The bondings of Zn, P, and Ti with Al and K suggest a predominantly terrigenous origin for them. The Pb-Cr-V-B group (elements probably included in the minerals of the heavy fraction), and Ag gravitate toward this terrigenous association. The bonding of Sn and Ca suggests a predominant presence of olivine in the plagioclase. The group Mg- Fe^{2+} -Mn-Na combines with the elements of the femic silicate admixture (subsiliic volcanic detritus

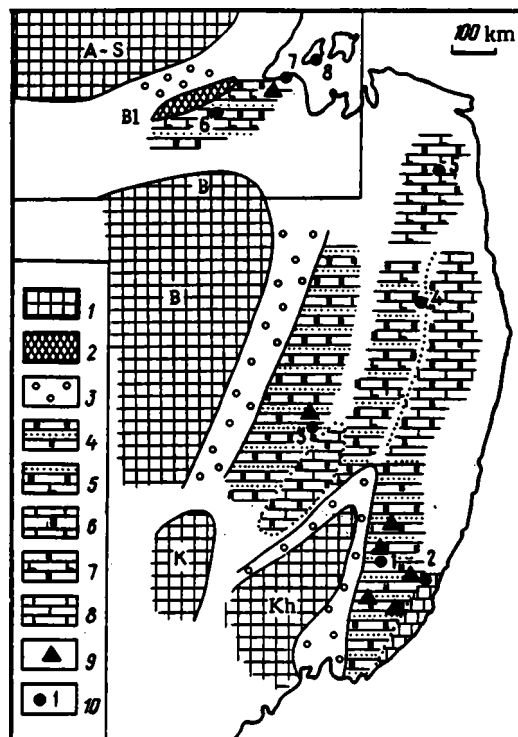


Fig. 3. Locations of sections studied on a diagram of the facies distribution for Middle Triassic to Lower Jurassic geosynclinal deposits of Sikhote-Alin (the locations of the sections of the Middle Paleozoic in the eastern portion of the Mongolian-Okhotsk region are shown in the insert): 1-3) regions adjacent to geosynclinal regions: 1) regions of denudation (A-S: Aldano-Stanovaya, B: Burenisk, K: Kenteisk, Kh: Khankaik), 2) Baladeysk protrusion-barrier (B1) dividing the Paleozoic miogeosynclinal Sevlinsk and eugeosynclinal Glavnii zone of the eastern portion of the Mongolian-Okhotsk region midway, 3) regions of occurrence of shelf terrigenous deposits of marginal troughs; 4-8) geosynclinal facies; 4) terrigenous-silicitic, 5) terrigenous-volcanic-silicitic, 6) carbonate-silicitic, 7) volcanogenic-silicitic (jasper), 8) limestone reef, 9) location of phtanite outcrop, 10) sections studied: 1) Ussuri River, 2) Rudnaya River, 3) Voronezh-2, 4) Dzhaur River, 5) Kiselevo, 6) Galam River, 7) Tyl' River, 8) Feklistova Island.

or its alteration products) and suggests a predominance of silicate forms of Fe^{3+} , rather than sulfide forms. The Ni-Co-Cu group are probably bound with authigenic sulfides. The unassociated Fe^{3+} and Mo do not show a preferential link with one of the groups and are apparently polygenic.

In the cherts of the northern Sikhote-Alin (sections at Voronezh-2, the Dzhaur River, and Kiselevo), one can identify the associations Al-K-B, Ti-Mn, Mg-Pb-Zn-V-Cr-Ga, Fe^{2+} -P-Sn-Cu-Ni-Co-Mo, and unassociated Ag, Ca, Na, and Fe^{3+} . The groundmass of boron is linked with K and Al and occurs in the terrigenous hydromicaceous admixture. The group Mg-Pb-Zn-V-Cr-Ga includes the majority of trace elements, and the link with Mg suggests their occurrence in femic detritus. The group Fe^{2+} -P-Sn-Cu-Ni-Co-Mo includes the majority of the most mobile trace elements, and the predominance of chalcophiles and bonding with Fe^{2+} suggests their predominant occurrence in authigenic sulfides. This group is closely linked to the Mg group. The latter reflects a genetic proximity: enrichment with hydrogenic iron and a complex of sorbed trace elements combined with an increase in the portion of mafic detritus in the admixture. Ag gravitates toward the Mg and Fe^{2+} groups but also toward the terrigenous group. The unassociated Ca, Na, and Fe^{3+} are apparently polygenic. The origin of the Ti-Mn link is unclear.

In contrast to cherts of the southern Sikhote-Alin collected from sections neighboring the Khankaissk massif, where linkage of the majority of the trace elements with clastics predominates, two-thirds of the samples from the sections at the Dzhaur River and Kiselevo furthest from the sialic massifs (paleoterrains) to the west consist of cherts. Here, the group of mobile trace elements linked with divalent iron, usually occurring in sulfides, stands out more distinctly in the cherts.

Jaspers (see Fig. 2c). The following groups can be distinguished: Al-K-Zn-Sn-Ni, Mg-Fe²⁺-B, Mn-Co-Cu-Pb-Ag-Ga, Fe³⁺-Ti-Cr-V-P-Mo, and unassociated Ca and Na. The association Zn, Sn, and Ni with Al and K suggests their linkage with clay impurities (hydromicas), possibly sorbing trace elements. Boron is linked with Fe²⁺ and Mg; this indicates its predominant occurrence in the femic fraction of the admixture rather than with the clays. The grouping of Co, Cu, Pb, Ag, and Ga with Mn but Ti, V, Cr, Mo, and P with Fe³⁺ allows us to connect these associations with selective sorption of trace elements by Fe and Mn. It is well known [21] that Ni, Cu, Co, and Pb are more energetically sorbed by manganese than by iron, while Cr, V, and Ti are typical accessory minerals to iron. Elements usually accumulated in oceanic ferromanganese concretions are linked with Mn in the jaspers. The elements of the Mn group are positively correlated with the elements of the aluminum group. These linkages usually arise within jaspers still on migration paths. In fluvial suspensions, Mn gravitates toward the finely pellic fraction of the suspension (0.01-0.001 mm), whereas Fe gravitates toward the subcolloidal [13, 21]. Ca negatively correlates with all of the elements and positively correlates only with volatiles, as a consequence of its occurrence in calcite (established by petrographic study of the jaspers). Na does not show link with one of the groups, but gravitates more toward Al.

Phtanites (see Fig. 2d). The following groups can be distinguished: Al-B, Ti-P-Fe³⁺, Fe²⁺-Mg-Mn, C_{org}-K-Na-Mo-Pb(?), Cu-V, Sn-Zn-Ni-Co-Cr-Ag, and Ca. In the phtanites, as in the cherts, boron is bound with the hydromicaceous fraction of the admixture. Ca and the group Ti-Fe³⁺-P combining elements in the minerals of the heavy fraction (titanomagnetite, sphene, apatite, and others) can also be classified as terrigenous. The group Fe²⁺-Mn-Mg combines the principal elements of the femic silicate admixtures and is negatively linked to the other groups. The weak link of C_{org} with the trace elements usually highly concentrated in the phtanites (V, Ag, Sn, and Cu) and its strong link with Na and K were unanticipated. Preferential linkage of C_{org} was noted only for Mo and Pb. The major portion of the trace elements (Sn, Zn, Ni, Co, Cr, and Ag) form a separate group with a predominance of chalcophiles; this group is not linked with C_{org}. The Cu-V association gravitates toward this group and also toward the Al group and, to a lesser degree, toward the C_{org} group. It is probably polygenic. The absence of linkage of the elements Ag, V, Cr, Cu, and B, enriching the carbonaceous silicites of Sikhote-Alin relative to the noncarbonaceous silicites, with C_{org} can be explained by the loss of carbon during catagenesis as a consequence of the breakdown of organometallic complexes, the redistribution of elements, and the evacuation of light hydrocarbons. The stronger linkage of K and Na with C_{org} than with Al probably reflects the connection of their formation with a change in the distributive provinces and a shift in the geographic range of the algae [8]. In contrast to the enclosing silicites, the phtanites and other rocks of the phtanitic batch contain exclusively hydromica in the silicate micaceous fraction. The arrival of other aluminosilicates to the radiolarian muds apparently did not foster the accumulation of organic material.

Clayey Cherts (See Fig. 2e). We distinguished the following associations: Al-K, Ti-V-Cr-B-P, Na-Ca-Mn-Zn, Mg-Fe²⁺, Sn-Pb-Cu-Ni-Co-Ga, Fe³⁺-Mo, and Ag. Ag and the group Ti-V-Cr-B-P, elements probably occurring in the minerals of the heavy fraction (ilmenite, chromspinel, apatite, and tourmaline) also of terrigenous origin, gravitate toward the terrigenous group Al-K linked with hydromicas. Apparently, Fe³⁺ and Mo are essentially terrigenous. The groups Na-Ca-Mn-Zn and Mg-Fe²⁺ linked with the femic silicate admixture and also the group Sn-Pb-Cu-Ni-Co-Ga containing the majority of chalcophiles present in authigenic sulfides stand in an antagonistic relationship to these terrigenous associations. As in the silicites, the femic silicate and authigenic sulfide groups are closely linked here, although the selections from these associations of elements included in the cherts and in the clayey cherts are somewhat different. In the clayey cherts, Fe²⁺ is linked with Mg, and predominates in the femic fraction of the admixture; but Fe²⁺ can also enter into the composition of the sulfide group in cherts. The poorly mobilized Cr and V are linked more with the terrigenous sialic admixture in the clayey cherts and with the femic silicate group in the cherts. In the latter, the differentiation of the poorly mobilized (Pb, Ga, Cr, and V) and mobile (Co, Mo, Cu, and Ni) trace elements is more distinct.

TABLE 4. Chemical Compositions of Cherts of Northern Sikhote-Alin

Oxides, %; trace ele- ments, 10 ⁻⁴ %	Suite			Oxides, %; trace elements, 10 ⁻⁴ %	Suite		
	Voro- nezh- (13/13)	Dzhaursk (11/11)	Kisel- evsk (10/12)		Voro- nezhsk (13/13)	Dzhaursk (11/11)	Kiselevsk (10/12)
SiO ₂	95.83	92.95	92.25	Zn	27	86	21
TiO ₂	0.20	0.20	0.19	Cu	48	101	79
Al ₂ O ₃	1.37	2.53	1.59	Ni	21	73	45
Fe ₂ O ₃	0.22	0.17	0.57	Co	5	12	9
FeO	0.79	1.89	2.27	Cr	11	26	23
MgO	0.08	0.46	0.27	V	18	58	25
CaO	0.14	0.67	0.91	B	39	35	20
MnO	0.03	0.03	0.04	Ag	0.04	0.06	0.03
K ₂ O	0.34	0.35	0.50	Mo	0.7	2.1	1.1
Na ₂ O	0.12	0.14	0.41	Ga	1.9	4.1	3.2
P ₂ O ₅	0.06	0.33	0.12	SiO ₂	92.5	86.9	88.3
Calcin. loss	0.63	0.13	0.73	Σ Fe	0.77	1.59	2.16
C _{org}	0.09	0.07	0.08	Al/(Al + Fe + Mn)	0.48	0.45	0.28
C _{carb}	0.00	0.03	0.01	K ₂ O/Na ₂ O	2.8	2.5	1.2
Sn	1.2	3.5	3.8	Fe ³⁺ /Fe	0.80	0.92	0.82
Pb	2.7	7	3.3				

Clayey Phtanites (see Fig. 2f). The following groups can be distinguished: Al-K-Mg, Ti-Pb, P-Cu-Cr-V-B-Mo-Ag, Fe²⁺-Mn-Sn-Zn-Ni-Co, Ca-Na, unassociated Fe³⁺ and C_{org}. The association Al-K-Mg and the groups Ti-Pb and Ca-Na gravitating to them are apparently of a terrigenous detrital origin. The majority of trace elements form two antagonistic groups: a phosphorous group and a divalent iron group. Nearly all of the trace elements enriching the carbonaceous silicites of the Sikhote-Alin, as opposed to those enriching the noncarbonaceous silicites, are concentrated in the phosphorous group. Organic carbon, which correlates negatively with all of the elements of the other groups, correlates positively (but insignificantly at the 5% level) with only some of the elements (V, Ag, and Mo) of this group. Elements which have usually low concentrations in carbonaceous silicites, predominately chalcophiles united by their common occurrence in authigenic sulfides, are included in the divalent iron group; Fe³⁺ is positively linked with P and Ca groups but gravitates more to the terrigenous group Ti-Pb, as in the phtanites. A femic silicate association of elements is absent in clayey phtanites as opposed to phtanites.

The correlated relationships between the elements reflect the genetically diverse composition of the components of the mineral admixture and show substantial differences within different lithological types of silicites. As a comparison of the cherts of southern and northern Sikhote-Alin indicates, parageneses of elements can differ significantly even within one and the same type of silicite.

Lateral Variation in the Chemical Compositions of the Silicites

The influence of the sedimentary environment upon the chemical composition of siliceous rocks was discovered [8] as a result of comparing Middle Triassic to Lower Jurassic silicites of Sikhote-Alin from sections located at various distances from sialic massifs (Khankaish, Bureinsk, etc.) serving as regions of erosion.

In northern Sikhote-Alin, the compositions of the Middle Triassic to Lower Jurassic deposits at distances from these massifs change from terrigenous-siliceous (Voronezh-2, Voronezhsk suite) to terrigenous-volcanic-carbonate-siliceous (Dzhaur River, Gur River, Dzhaursk suite) and, further along, to volcanic-siliceous (North Kiselevo, Kiselevsk suite) as one proceeds from southwest to northeast (see Fig. 3). The relationships between lithological types of siliceous rocks change simultaneously in the siliceous beds. Packets of phtanites and clayey phtanites coincide with beds of chert in terrigenous-siliceous facies, where jaspers are rare. Carbonaceous silicites are absent in the Dzhaursk Suite, but jaspers are present, constituting 7-10% of the volume of the silicites; they constitute 60-70% of the volume of silicites in the Kiselevsk Suite. Cherts occur in all three sections and can therefore be used for comparisons (Table 4).

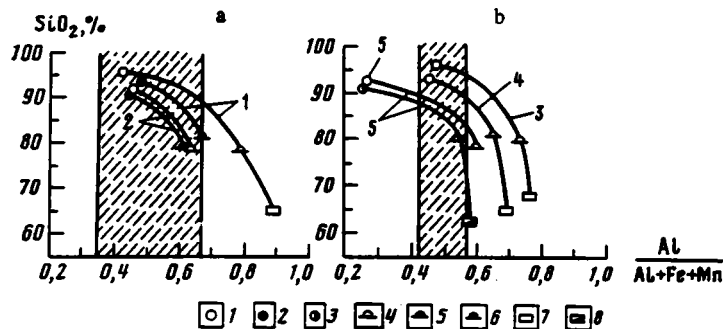


Fig. 4. Positions of regression lines for $Al/(Al + Fe + Mn)$ upon SiO_2 in argillitic-siliceous parageneses of the Triassic-Lower Jurassic (a) and northern Sikhote-Alin (b). Rocks: 1) cherts, 2) phtanites, 3) jaspers, 4) clayey cherts, 5) clayey phtanites, 6) clayey jaspers, 7) grey argillites, 8) red hematite-bearing argillites. Lines of regression with respect to the average compositions of the rocks from the sections: 1) Ussuri River, 2) Rudnoi River, 3) Voronezh-2, 4) Dzhaurs River, 5) Kiselevo. Hatched region) interval of values for $Al/(Al + Fe + Mn)$ in the associated Triassic-Jurassic volcanic rocks of the early geosynclinal complex.

The average contents of SiO_2 and SiO_2 (free) in cherts of the Dzhaursk and Kiselevsk suites are similar but lower than in the Voronezhsk Suite; Ti and Mn are identical in all of the sections; Co_{org} is less than 0.30%, and carbon is absent. Fe/Al equals 1.06, 1.19, and 2.57 respectively in cherts of the Voronezhsk, Dzhaursk, and Kiselevsk suites. The Dzhaursk and Kiselevsk suites are enriched with respect to Fe relative to the Voronezhsk Suite and impoverished with respect to not only chert but also with respect to clayey cherts and the argillites linked to them. The values of the $Al/(Al + Fe + Mn)$ modulus in the argillitic-siliceous associations are higher in rocks of the Voronezhsk Suite and lower in the Kiselevsk Suite (Fig. 4). The proportion of sodium in the total alkalis increases in parallel with the increase in iron content within the cherts (Fig. 5). The K_2O/Na_2O values in the cherts of the Voronezhsk, Dzhaursk, and Kiselevsk suites average 2.8, 2.5, and 1.2 respectively. The dependence of K_2O/Na_2O upon $Al/(Al + Fe + Mn)$ in the silicites of Sikhote-Alin and the Mongolian-Okhotsk region (see Fig. 5 [8]) reflect a tendency toward parallel increases in the contents of authigenic iron and femic-silicate detritus enriched in Na within the admixture. The value of the $Al/(Al + Fe + Mn)$ modulus shows a hyperbolic dependence upon SiO_2 in rocks of the terrigenous-siliceous series (see Fig. 4), often occurring in rhythmical interbedding. In a significant portion of the silicites, this modulus is lower than in the basaltoids of the geochemical complexes. Therefore, its lower values in highly siliceous silicites are assured not so much by the femic content of the silicate fraction as by the high content of authigenic iron minerals in the admixture.

The decrease in the content of alumina and potassium and the increase in iron and sodium in the silicites from the sections further from the Bureinsk and Khankaish sialic massifs reflect a decrease in the influence of continental land and an increase in the influence of an intrageosynclinal source upon the composition of the admixtures in the siliceous formed; this is associated with a circum-continental zoning.

In the cherts of the Voronezhsk Suite, the content of several trace elements (Ga, Sn, Cu, Cr, and Ni) are significantly lower than in the cherts of the Dzhaursk and Kiselevsk suites (see Table 4). The value K_2 (equaling $El/Al_{silic}:El/Al_{silic}$) used to compare the contents of elements in the admixture shows an impoverishment of B, Ti, and Ag in the silicites of the Dzhaursk and Kiselevsk suites ($K_2 < 1$) and an enrichment with the majority of the remaining elements ($K_2 > 1$) in comparison to the cherts of the Voronezhsk Suite:

Dzhaursk/Voronezhsk

B.	Ti	Mn	Ag	Fe	Cu	Ga	Co	Cr	Pb	Mo	Sn	Zn	V	Ni	P
0.5	0.6	0.9	1.1	1.15	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9	3		

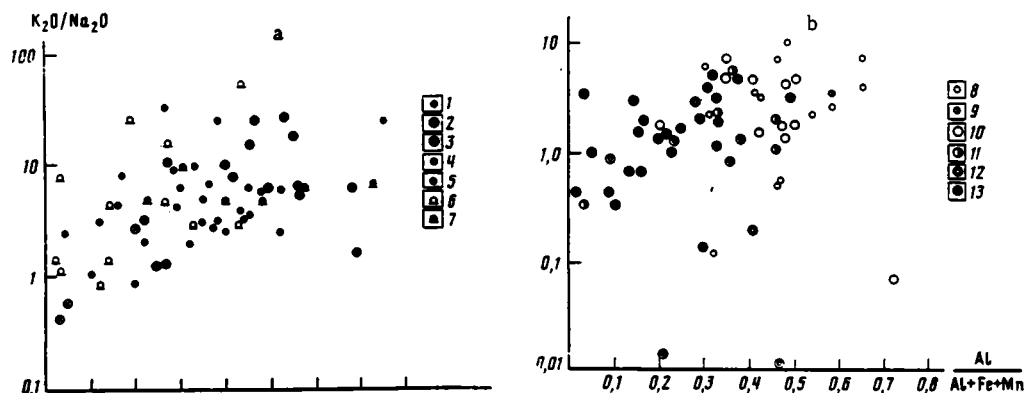


Fig. 5. Dependence of K_2O/Na_2O upon $Al/(Al + Fe + Mn)$ in the silicites of Sikhote-Alin (a: southern and central Sikhote-Alin; b: northern). 1) cherts (T_3), Sadovaya River; 2) cherts (T_{2-3}), N. Uborka-Ogorodnaya River; 3) phtanites (T_2), Ogorodnaya River; 4) cherts (T_3), Zhuravlevka River; 5) cherts (J_{1-2}), Uborka settlement-Koksharovka settlement; 6) cherts (T_2-J_1), Greater Ussuri River at Dal'nii Kut; 7) phtanites (T_2), Greater Ussuri River at Dal'nii Kut; 8) cherts of the Voronezhsk Suite (T_2-J_1), Voronezh-2 settlement; 9) jaspers of the Voronezhsk Suite (T_2-J_1), Voronezh-2 settlement; 10) cherts, Dzhaursk Suite (T_2-J_1), Dzhaursk River; 11) jaspers, Dzhaursk Suite (T_2-J_1), Dzhaursk River; 12) cherts, Dzhaursk Suite (T_3-J_1), Kiselevo; 13) jaspers, Kiselevsk (T_3-J_1), Kiselevo.

Kiselevsk/Voronezhsk

B	Zn, Ag	Ti	V, Mn, Pb	Mo	Co	Ga	Cu	Ni	P, Cr	Fe	Sn
0.5	0.7	0.8	1.1	1.2	1.3	1.4	1.5	1.7	1.9	2.4	2.8

Kiselevsk/Dzhaursk

Zn	P, V	Mo, Pb, Ag	Ni	B	Co	Ga	Cu	Cr	Ti	Sn	Mn	Fe
0.4	0.6	0.8	0.9	1	1.1	1.2	1.3	1.4	1.5	1.8	1.9	2.2

In the cherts of the Kiselevsk Suite as compared to the cherts of the Dzhaursk Suite, the admixture contains more Co, Ga, Cu, Cr, Ti, Sn, Mn, and Fe and less Zn, P, V, Mo, Pb, Ag, Ni, and B. The elements enriching the admixture in the cherts of the Kiselevsk Suite ($K_2 > 1$) are primarily femic and concentrated in the basaltic detritus; they include the poorly mobilized elements Fe, Ga, Cr, and Ti, and also the mobile elements Sn, Co, and Cu. Depleted in the admixture ($K_2 < 1$) are the elements of the sialic rocks (Mo, Ag, Pb, and Zn) and those which are highly concentrated in the carbonaceous silicites (P, V, Mo, Ag, B, and Pb), i.e., elements which could accumulate as a result of organic matter. The role of the latter is probably greater in the more shoreward areas of the sea. Changes in the chemical composition are accompanied by analogous changes in the mineral and chemical compositions of the terrigenous rocks paragenetically associated with them and with the overall facies changes in the Middle Triassic to Lower Jurassic deposits. They suggest a dual supply of silicate admixture to a basic of silicic buildup: from sialic terrain and from an intra-geosynclinal source (basaltic structures). A circum-continental zonation is responsible for the lesser inflow of sialic detritus, the greater inflow of mafic detritus, and, also, the greater contribution of hydrogenic iron to the radiolarian mud accumulating at an appreciable distance from the sialic land.

A lateral zonation in the chemical composition of the Middle Triassic to Lower Jurassic silicites was discovered in the southern portion of the region, in a field where terrigenous-siliceous facies occur, during a comparison of sections along the right bank of the Ussuri River south of N. Koksharovki and along the Rudnoi River and at Dal'negorsk (see Fig. 3). The siliceous beds are characterized by similar structure and collection of lithological types of rocks (cherts, phtanites, clayey cherts, and clayey phtanites) and, apparently, are similar with respect to sedimentary environment. However, the section at Dal'negorsk is situated approximately 100 km east of the section along the Ussuri River, i.e., further away from the Khanka Massif and other sialic blocks, where land existed. The average petrochemical compositions for each type of silicite along the sections are generally similar, with the exception of the higher SiO_2 content in the sample of chert from the Ussuri River.

TABLE 5. Average Chemical Composition of Middle Triassic to Lower Jurassic Silicites of Southern Sikhote-Alin

Oxides, %; trace elements, 10 ⁻⁴ %	Sections							
	Ussuri River (south of Koksharovka)				Rudnaya River, (Dal'negorsk, Sodovyi)			
	cherts (9/29)	phtanites (9/13)	clayey cherts (4/15)	clayey phtanites (9/11)	cherts (9/9)	phtanites (8/8)	clayey cherts (11/11)	clayey phtanites (11/11)
SiO ₂	95.01	92.39	77.87	82.23	91.88	91.60	79.27	81.85
TiO ₂	0.11	0.18	0.54	0.39	0.09	0.09	0.41	0.32
Al ₂ O ₃	1.59	2.06	11.10	5.68	3.16	2.83	9.25	6.81
Fe ₂ O ₃	0.35	0.95	1.84	1.65	0.35	0.44	0.83	1.09
FeO	1.17	0.72	0.59	0.52	2.25	1.89	3.20	1.97
MgO	0.43	0.21	1.03	0.65	0.61	0.37	1.58	1.26
CaO	0.19	0.10	0.01	0.04	0.15	0.18	0.45	0.47
MnO	0.07	0.03	0.03	0.02	0.09	0.03	0.10	0.06
K ₂ O	0.32	0.64	2.29	1.10	0.39	0.56	1.56	1.63
Na ₂ O	0.15	0.07	0.07	0.12	0.07	0.07	0.25	0.13
P ₂ O ₅	0.12	0.21	0.71	0.42	0.06	0.07	0.05	0.13
Calcin. loss	0.19	2.12	3.48	6.70	0.57	1.35	2.59	3.68
Corg	0.05	1.06	0.06	2.26	0.09	0.28	0.10	1.59
Ccarb	0.004	0.00	0.00	0.00	0.01	0.00	0.004	0.00
Sn	2.8	3.7	3.1	3.5	2.7	2.8	3.2	4.1
Pb	5.9	10.5	11.8	18.2	16.1	38.1	14.8	31.2
Zn	40	35	79	28	170	197	154	172
Cu	56	92	59	120	71	103	60	76
Ni	30	35	36	29	57	54	42	40
Co	6.5	5	7	3	20	17	11	5
Cr	18	41	55	84	38	50	42	63
V	31	196	119	402	45	294	80	441
B	24	61	108	211	25	38	63	41
Ag	0.13	1.48	0.04	1.76	0.23	1.15	0.15	0.78
Mo	1.4	24	2.3	70	2	20	2.3	85.5
Ga	2.4	—	7.5	—	4.7	6.5	8.7	15.7
SiO ₂	91.2	87.5	51.3	68.4	84.3	84.8	57.1	65.5
Fe	1.15	1.22	1.75	1.56	1.99	1.78	3.07	2.29
Al/(Al+Fe+ +Mn)	0.41	0.47	0.77	0.66	0.45	0.45	0.61	0.60
K ₂ O/Na ₂ O	2.1	9.1	32.7	9.2	5.6	8.0	6.2	12.6
Fe ³⁺ /Fe	0.79	0.45	0.26	0.26	0.88	0.83	0.81	0.67

The silicites at Dal'negorsk are enriched in Fe, Mg, Ca, and Mn and trace elements in comparison with the untypical silicites along the Ussuri River (Table 5). The values of the Al/(Al + Fe + Mn) modulus in the clayey cherts and cherts average lower than in the silicites of Dal'negorsk (see Fig. 4). The portion of silicic clastics in the admixture in the silicites of Dal'negorsk is lower and contents of femic detritus, authigenic iron minerals, and trace elements sorbed by iron are higher than in the untypical rocks along the Ussuri River. The usually high contents of Pb and Zn in the silicites at Dal'negorsk could probably have been caused by a later hydrothermal or hypogene contamination of rocks in a region where ore shows and deposits of these metals are present.

A significant lateral variation in the chemical composition of the silicites was discovered within the Mongolian-Okhotsk region in Silurian-Lower Devonian and Devonian-Lower Carboniferous deposits [9]. The lower values of Al/(Al + Fe + Mn) and K₂O/Na₂O in silicites from the sections at the Tyl' River and the Feklistova Island in comparison with the section at the Galan River (see Table 3) are connected with their great distance northeast of the Burenisk massif. The influence of the Sikhote-Alin terrain was weakened by the Baladevsk barrier situated along the northern border of the geosynclinal trough. The contents of the majority of trace elements in the silicites within the northern sections (see Table 3) increase simultaneously with increases in the content of Fe and Na and decreases in the content of Al and K. The majority of the jaspers occur in the Mongolian-Okhotsk region; they were sampled within the section at the Galan River, near the Burenisk massif, since jaspers are rare in the sections at the Tyl' River and Feklistov Island further east. Cherts predominate at these latter sites, constituting a significant portion of the total sample. Therefore, the average contents of Fe and trace elements in the cherts of the region are higher than in the jaspers (see Table 3).

The lateral changes in the chemical composition of the silicites of the Mongolian-Okhotsk region are also connected with a circum-continental zonation, a zonation which has a greater influence upon the chemical composition than does the environment of diagenesis

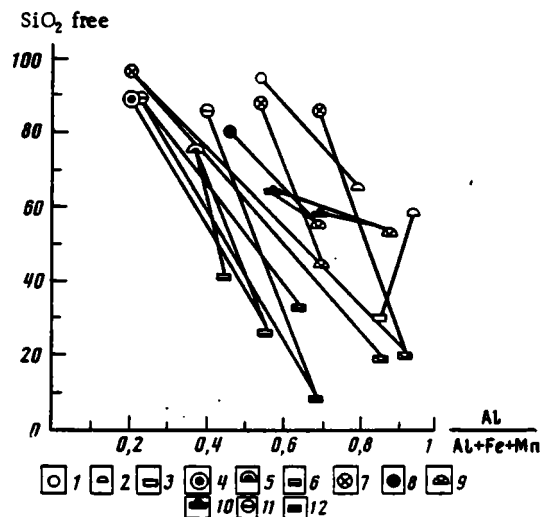


Fig. 6. Dependence of the $Al/(Al + Fe + Mn)$ modulus upon SiO_2 (free) in mixed elements of elementary cyclites in the rhythmically layered beds of Sikhote-Alin. 1-3) Voronezhsk Suite: 1) cherts, 2) clayey cherts, 3) argillites; 4-6) Kiselevsk Suite: 4) jaspers, 5) clayey jaspers, 6) red argillites; 7-10) Él'dovaksk bed (Uborka settlement - Ogorodnaya River): 7) cherts, 8) phtanites, 9) clayey cherts, 10) clayey phtanites; 11-12) Samarkinskaya bed (J_1 - J_2): 11) cherts, 12) argillites.

(oxidizing or reducing) or even the hydrothermal activity widely manifest here during epochs of silicic buildup [8]. Exhalation-hydrothermal iron ores are widely distributed in the southwestern portion of the zone and usually lie within jaspers or between subadjacent tuffs and lavas of basaltic prophyrites and jaspers [2]. Nevertheless, the jaspers and cherts in this portion of the zone (the Galam River) are considerably more impoverished in iron and trace elements than in the northeastern portion (the Tyl' River and Feklistov Island), where iron ores are almost absent. As already observed [8, 9], the cause of the weak influence of the ore hydrotherms on the chemical composition of the silicites consists in their transience and incomparably smaller scale of the endogenous efflux in comparison with the biogenic silicic buildup in this zone: the volume of Fe and Mn ores is more than 600 times less than the volume of the silicites. As in Sikhote-Alin, a lateral zonality is reflected in the compositions of the mineral admixtures (of the clay admixtures, in particular) in the silicites [7], in the contents of rock-forming oxides and trace elements within the lithological types of siliceous rocks, and in the terrigenous rocks paragenetically associated with them [9, 16].

Geochemical Criteria for Correlating Siliceous Strata and Paleogeographical Reconstructions

The lateral variation in the chemical compositions of the silicites discovered in Sikhote-Alin and the Mongolian-Okhotsk regions and noted also in the Upper Jurassic silicites of Turkey [38] is similar to the circum-continental zonality well known in modern sediments of oceanic basins. Therefore, the criteria suggested by M. Steinberg and M. Mpodozis [37] can be used to establish the relative "pelagic nature" or "precontinental nature" of the cherts from various sections of one stratum, especially if not only individual silicites but all members of the terrigenous-siliceous association (argillite-clayey silicite-silicite) are compared. However, variations in the models of Fe/Al , $Al/(Al + Fe + Mn)$, and K_2O/Na_2O in the silicites of each of the sections being compared leads to a significant overlap of points on graphs and is responsible for the low statistical significance associated with the differences in average values.

In the mixed elements of cyclites with siliceous layers 0.5-15 cm (usually 2-6 cm) thick and clay layers 0.2-30 mm (usually 1-10 mm) thick, the fluctuations in the $Al/(Al + Fe + Mn)$ modulus are significant (Fig. 6) and overlap the range of values of the modulus for modern sediments from the precontinental (marginal seas, hemipelagic zones of the ocean, deep-water trenches of the oceans and the metalliferous muds of the mid-oceanic rises [37]). Lithological and geochemical investigations in the Sikhote-Alin region [7, 8] have shown that a simple

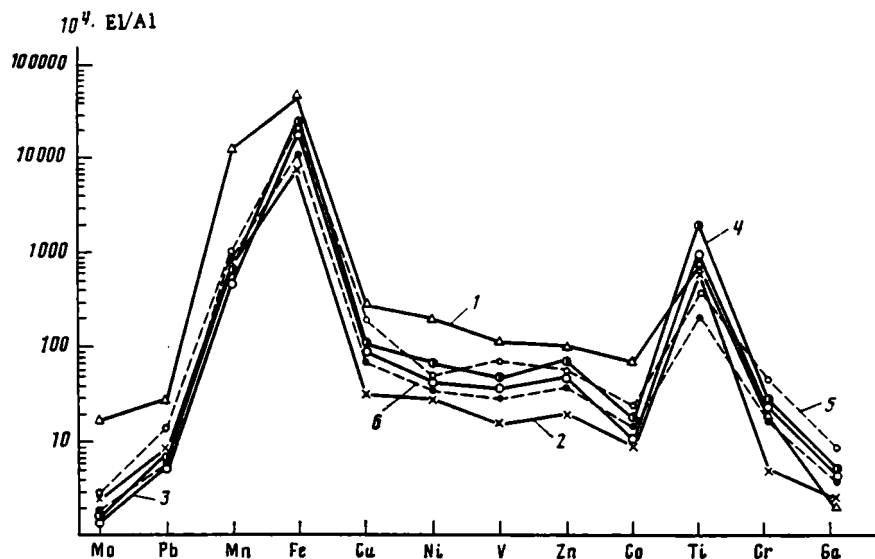


Fig. 7. Ratio of average contents of elements to aluminum in the silicites of Sikhote-Alin, the Mongolian-Okhotsk region, the metalliferous sediments of the East Pacific Rise, and the deep-water clays of the Pacific Ocean: 1) metalliferous sediments (according to [15]); 2) deep-water clays (according to [39]); 3-4) Sikhote-Alin (3: cherts, 4: jaspers); 5-6) Mongolian-Okhotsk region (5: cherts, 6: jaspers).

recurrence cycle of this nature could be caused by a periodic, pulsed delivery of terrigenous material at the moments of formation of the clay elements in the cycles, with the delivery proceeding against a background of uninterrupted slow sedimentation of radiolarian skeletons. During the long intervals of time when the siliceous layers are being formed, a trace amount of background silicate suspension is mixed with a commensurate amount of hydrogenic iron; this is what is responsible for the low values of $Al/(Al + Fe + Mn)$ in these layers. The paleogeographic environments could not change with a hundred- or thousand-year periodicity in such a fundamental fashion as to cause the fluctuations in the modulus associated with the mixed elements in the cyclites. Therefore, the primary regulator of the compositions of the admixtures in silicite-argillite parageneses, a regulator affecting the magnitude of $Al/(Al + Fe + Mn)$ and other geochemical coefficients, is the terrigenous supply, the regime of which can vary significantly over time. This calls into question assertions [10] of an invariance of geochemical associations in siliceous and clayey elements within the cyclites of rhythmically layered siliceous packets.

The combined effects of the circum-continental zonation and the cyclicity of the sedimentation upon the chemical composition of the siliceous rocks significantly restrict the possibilities of using geochemical data for stratigraphic correlations of "barren" siliceous strata. Parageneses of elements could be similar in different strata and differ within a single stratum depending upon the distance of the sources of the admixture material from the sites of sedimentation, the regime of delivery of such material, and the paleogeographic circumstances surrounding the sedimentation.

The siliceous strata of Sikhote-Alin, the Mongolian-Okhotsk region, and many other Phanerozoic folded regions accumulated in near-continental basins: marginal seas, deep-water trenches, back-arc basins, on continental slopes, the adjacent portions of the abyssal plain of the oceans or in "young oceans" of the type represented by the Gulf of California [8, 25, 34]. In these environments, beds of radiolarian silicites could be formed in the presence of an extremely low supply of terrigenous material. In the Middle-to-Late Triassic and Early Jurassic, when the thickest siliceous strata of Sikhote-Alin, Sakhalin, and Japan were deposited on the adjacent land (the Bureinsk and Khanka massifs), nature surface weathered kaolinite crusts were formed on the Aldan Shield and in other locations in Mongolia, and the peneplain had long been in existence [17, 18, 22]. The structure of the river drainage differed from the modern drainage in the marginal seas with respect to having lower drift of solid and dissolved substances relative to the greater role of solvents and colloids. This

was apparently connected with the enrichment of the admixture in the silicites with hydro-genic iron and trace elements, as though the ancient near-continental environments resembled modern pelagic environments in this respect.

Differences from the pelagic muds can be seen nevertheless. A comparison of the El/Al values in the siliceous rocks of Sikhote-Alin and the Mongolian-Okhotsk region with the deep-water red clays and metalliferous sediments of the Pacific Ocean indicates a similarity in the chemical compositions of the admixtures in the silicites of both regions; the comparison also shows that both silicites are more enriched in Fe, Cu, Ni, V, An, and Co than are deep-water muds and that both silicites are less enriched in these elements than metalliferous sediments (Fig. 7). The poorly mobilized elements Ga and Cr (and Ti in Sikhote-Alin) within the silicites are concentrated in the admixture more than in the clays and metalliferous muds, while Mn, Mo, and Pb, on the other hand, enrich pelagic clays and especially metalliferous deposits. These differences are connected with the near-continental depositional environment of the cherts and jaspers of both regions during the epoch of diminutive supply of terrigenous clastic material and, as a consequence, the near-continental nature of the accumulation, i.e., the insufficiently developed differentiation of poorly mobilized and mobile elements in silicites.

The cyclical nature of geochemical processes has no less of an influence than the dimensions of basins upon the structure of fluvial drainage and the geochemical characteristics of the suspension, and, consequently, upon the composition of the admixtures in siliceous muds. This limits the possibilities of using geochemical criteria for paleogeographical and paleotectonic reconstructions in folded regions. Their use for this purpose is possible when comparing strata formed during one and the same epoch in one and the same basin.

LITERATURE CITED

1. S. G. Ankinovich and E. A. Ankinovich, "Conditions of accumulation and formation of ore-bearing schists of the Lower Paleozoic in Southern Kazakhstan," in: *The Geochemistry of Sedimentary Rocks and Ores* [in Russian], Nauka, Moscow (1968), pp. 356-376.
2. G. I. Arkhipov and E. A. Panskikh, "Basaltoid magmatism and iron accumulation in the Dzhagdinsk geosyncline," in: *Problems of Magmatism and Tectonics in the Far East* [in Russian], Far-East Scientific-Research Center, Academy of Sciences of the USSR (1975), pp. 56-67.
3. G. I. Burii, "Triassic conodonts in the siliceous strata of Sikhote-Alin," *Tikhookean. Geol.*, No. 2, pp. 100-104 (1985).
4. V. S. Vishnevskaya, *Radiolarites as Analogs of Modern Radiolarian Muds* [in Russian], Nauka, Moscow (1984).
5. I. I. Volkov and L. S. Fomina, "Trace elements in the sapropelic muds of the Black Sea and their interconnection with organic matter," *Litol. Polezn. Iskop.*, No. 6, 3-15 (1971).
6. I. I. Volkov, "Chemical elements in fluvial drainage and their delivery to the sea," in: *Problems of the Lithology and Geochemistry of Sedimentary Rocks* [in Russian], Nauka, Moscow (1975), pp. 85-113.
7. Yu. G. Volokhin, "Clay minerals of the geosynclinal siliceous rocks of the Paleozoic and Mesozoic in the southern Far East," *Geochemistry and Petrochemistry of Sedimentary Complexes in the Far East* [in Russian], Far-East Scientific-Research Center, Academy of Sciences of the USSR, Vladivostok (1980), pp. 76-99.
8. Yu. G. Volokhin, *Siliceous Rocks of Sikhote-Alin and the Problem of the Origin of Geosynclinal Siliceous Strata* [in Russian], Far-East Scientific-Research Center, Academy of Sciences of the USSR, Vladivostok (1985).
9. I. N. Govorov, M. A. Mikhailov, Yu. G. Volokhin, et al., "Geochemistry of Platformal and Geosynclinal Sedimentary Rocks and Ores [in Russian], Nauka, Moscow (1983), pp. 145-157.
10. V. N. Konditerov, T. V. Dominikovskaya, V. F. Sorokin, and A. D. Petrovskii, *Geological Surveying in Regions of Occurrence of Siliceous Formations* [in Russian], Nedra, Leningrad (1981).
11. G. S. Konovalov, A. A. Ivanova, and T. Kh. Kolesnikova, "Trace and rare elements dissolved in water and contained in the suspended matter of the chief rivers of the USSR," in: *Geochemistry of Sedimentary Rocks and Ores* [in Russian], Nauka, Moscow (1968), pp. 72-87.

12. N. A. Lisitsyna, "Geochemistry of the weathered crusts," in: *Geochemistry of Sedimentary Rocks and Ores* [in Russian], Nauka, Moscow (1968).
13. I. Yu. Lubchenko and I. V. Belova, "Migration of elements in fluvial waters," *Litol. Polezn. Iskop.*, No. 2, 23-29 (1973).
14. A. O. Mazarovich, *Tectonic Development of Southern Primor'ya in the Paleozoic and Early Mesozoic* [in Russian], Nauka, Moscow (1985).
15. A. A. Migdisov, Yu. A. Bogdanov, A. P. Lisitsyn, et al., "Geochemistry of metalliferous sediments," in: *Metalliferous Sediments of the Southeastern Portion of the Pacific Ocean* [in Russian], Nauka, Moscow (1979), pp. 122-200.
16. M. A. Mikhilov and Yu. G. Volokhin, "Petrochemical composition of sandstones of the Paleozoic in the eastern portion of the Mongolian-Okhotsk folded region," in: *Geology of the Continental Margins* [in Russian], Far-East Scientific-Research Center, Academy of Sciences of the USSR, Vladivostok (1979), 72-74.
17. V. P. Petrov, *Principal Considerations Concerning Ancient Weathered Crusts* [in Russian], Nedra, Moscow (1967).
18. V. P. Petrov, "Ancient weathered crust and relict planes of discontinuity in Mongolia," *Izv. Akad. Nauk USSR, Ser. Geol.*, No. 2, 87-98 (1985).
19. I. F. Nikitin and A. I. Zamoid (eds.), *Applied Stratigraphy* [in Russian], Nedra, Leningrad (1984).
20. B. I. Smirnov, *Correlational Methods for Paragenetic Analysis* [in Russian], Nedra, Moscow (1981).
21. N. M. Strakhov, *Problems of the Geochemistry of Modern Oceanic Lithogenesis* [in Russian], Nauka, Moscow (1976).
22. V. A. Tashchilkin, "The weathered crusts of Primor'ya," Dissertation, Institute of Geology of Ore Deposits, Petrography, Mineralogy, and Geochemistry, Academy of Sciences of USSR, Moscow (1969).
23. I. V. Khvorova, "Silicic accumulation in geosynclinal regions of the past," *Tr. Geol. Inst. Nauk, SSSR*, No. 196, 9-136 (1968).
24. I. V. Khvorova, B. P. Zolotarev, and A. I. Gusareva, "Trace elements in eugeosynclinal siliceous rocks of the Southern Urals," *Litol. Polezn. Iskop.*, No. 6, 26-41 (1972).
25. I. V. Khvorova, "Eugeosynclinal silicic accumulation and its distinction from the oceanic," *Marine Geology, Sedimentology, Sedimentary Petrography, and Geology of the Ocean* [in Russian], Internat. Geol. Congress, 26th session. Reports of Soviet Geologists, Nedra, Leningrad (1980).
26. V. N. Kholodov, *Sedimentary Ore Genesis and Metallogenesis of Vanadium* [in Russian], Nauka, Moscow (1973).
27. Ya. É. Yudovich, *Geochemistry of Commercial Coals* [in Russian], Nauka, Leningrad (1980).
28. Ya. É. Yudovich, *Regional Geochemistry of Sedimentary Strata* [in Russian], Nauka, Leningrad (1973).
29. M. Baltuck, "Provenance and distribution of Tethyan pelagic and hemipelagic siliceous sediments, Pindos Mountains, Greece," *Sedimentary Geol.*, 31, No. 1, 63-88 (1982).
30. K. Boström, M. N. Peterson, O. Joensuu, and D. Fisher, "The origin of aluminum-poor ferromanganous sediments in areas of high heat flow in the East-Pacific Rise," *Marine Geol.*, 7, 427-447 (1969).
31. K. Boström, T. Kraemer, and S. Gartner, "Provenance and accumulation rates of opaline silica, Al, Ti, Fe, Mn, Cu, Ni, and Co in Pacific pelagic sediments," *Chem. Geol.*, 11, 123-148 (1973).
32. E. R. Cressman, "Data of geochemistry: nondetrital siliceous sediments," *U.S. Geol. Surv. Prof. Paper*, 440, 1-22 (1962).
33. J. R. Hein, E. P. Kuijpers, P. Denyer, and R. E. Sliney, "Petrology and geochemistry of Cretaceous and Paleogene cherts from western Costa Rica," in: *Siliceous Deposits in the Pacific Region*, Elsevier, Amsterdam, Oxford, New York (1983), pp. 143-174.
34. J. R. Hein and S. M. Karl, "Comparisons between open-ocean and continental margin chert sequences," in: *Siliceous Deposits in the Pacific Region*, Elsevier, Amsterdam-Oxford-New York (1983), pp. 25-43.
35. J. H. Martin and G. A. Knauer, "The elemental composition of plankton," *Geochim. Cosmochim. Acta*, 37, 1639-1653 (1973).
36. C. Rangin, M. Steinberg, and Ch. Bonnot-Courtois, "Geochemistry of Central Baja California (Vizcaino-Cedros-San Benito): implication for paleogeographical reconstruction of an old oceanic basin," *Earth Planet. Sci. Lett.*, 54, 2, 313-322 (1981).
37. M. Steinberg and M. C. Mpodozis, "Classification géochimique des radiolarites et des sédiments siliceux océanique, signification paléocéanographique," *Oceanol. Acta*, 1, 3, 359-367 (1978).

38. M. Steinberg, C. Bonnot-Courtois, and S. Tlig, "Geochemical contribution to the understanding of bedded chert," in: Siliceous deposits in the Pacific region, Elsevier, Amsterdam-Oxford-New York (1983), pp. 193-210.
39. K. Turekian and K. H. Wedepohl, "Distribution of the trace elements in some major units of the Earth's crust," Bull. Geol. Soc. Am., 72, No. 2, 175-191 (1961).
40. D. Wachs and J. R. Hein, "Petrography and diagenesis of Franciscan limestones," J. Sediment. Petrol., 44, No. 4, 1217-1231 (1974).

A SUPPLEMENT TO THE QUESTION OF THE IMPORTANCE OF THE BIOGENIC
FACTOR IN THE FORMATION OF PHOSPHORITES

N. V. Shabanina

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In an example of middle Eocene granular phosphorites from Central Kyzylkum, it is shown that the main part of the phosphatic formations is phosphatized organic remnants and the products of their life activity. The morphostructural features of the phosphatic components are caused by the morphological forms of the organisms.

The question of the importance of biogenic factors and the life activities of organisms in phosphorite formation are repeatedly discussed in the literature. The author thinks it possible to reflect on this again in connection with data obtained as a result of studying the material composition of middle Eocene granular phosphorites from Central Kyzylkum, which have been investigated in many articles [4, 14-16, 21, 22, 25, 28, 30].

The granular phosphorites of Central Kyzylkum are distinctive natural formations; accumulations of a huge quantity of phosphatized remnants of different invertebrates: foraminifers, pelecypods, gastropods, worms, enichoderms, ostracods, and others, with a subordinate quantity of boney detritus from vertebrates in the form of scales, teeth, vertebrae, fragments of different bones, and coprolites. They are concentrated mainly in two commercial layers (I and II), with an average thickness of 0.6 and 0.9 m respectively, and correlated to the clay-marl sequence of middle Eocene. In addition to these, four thin (0.05-0.3 m) layers of phosphorites, the "basal," "null," III, and IV layers, are present in Eocene deposits. The layers, which have a horizontal or weakly sloping attitude and areal development, are distributed in the Central Kyzylkum territory in several Mesozoic synclinal structures, bounded by Paleozoic uplifts.

With the goal of detailed study of the mineralogic-petrographic features of granular phosphorites, the author processed more than 2000 samples of phosphorites and surrounding rocks, applying a complex of methods (study of hand specimens, thin sections, immersion specimens, washing out of phosphorites, dispersing on sieves, study of fractions and monosamples). The following conclusions are a result of the study.

1. The useful component of the rocks is fluorocarboapatite concentrated mainly in the granular portion of rocks, represented by phosphatic biomorphozoa (replacement and infilling) of the invertebrates listed above, amid which foraminifera predominated.
2. Every stage of their replacement by phosphate, from initial to complete, is traceable in thin sections.
3. The bony detritus of vertebrates and coprolites are a constant and compulsory component of the phosphatic granular material of phosphorites.
4. Phosphatic biomorphozoans contain abundant carbonate nannoplankton, some part of which is replaced by phosphate. Nannoplankton compose the greatest part of the clay-limestone pelitomorph cement of the phosphorites, and with foraminifera they are the rock forming carbonate component of the clay-marl rocks which surround the phosphorites.
5. The complex of organic remnants in the phosphorites and surrounding rocks represents a food chain: nannoplankton as the simplest (mollusks etc.), and vertebrates, which makes it possible to judge the high biological productivity of the territory's phosphorite formation.

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6. Various other phosphatic components (oolites, pseudoolites, and nodules) comprise no more than 10-15% of the total quantity of phosphatic formations. In addition, components which are present (from several percent up to 15-20%), that do not have the characteristic signs of biomorpha, such as oolitic structures, etc., may be defined as phosphatic "grains". Study under binocular, in thin sections, and immersed samples showed that the greatest portion of them represent fragments of the above listed biomorpha, which have lost their characteristics as a result of breakdown and rounding. Sh. Zhuraev [13] first drew a similar conclusion on the origin of phosphatic "grains" in granular middle Eocene phosphorites of the southwestern extensions of the Gissarsk ridge. A portion of the "grains" has a coprogenic origin; within the "grains" are transformed completely phosphatized shells of foraminifera. To various degrees, phosphatized organic remnants (of foraminifera, less often others) are the nuclei of the majority of oolites; they are also contained in great quantity in the grains which have organic and relict-organic structure.

On the basis of data from investigators studying the phosphorites of other regions of Central Asia, beginning in the 30's (articles by K. S. Andrianov, B. A. Petrushevskii, and others) up to the present time (articles by V. Ya. Il'yashenko, Sh. Zhuraev, V. V. Oleinik, N. P. Petrov, M. Dzhanelilov, etc.), the phosphatized remnants of different organisms are always present along with nodules and grains in Cretaceous-Paleogene phosphorites; they are also constant components of the Cretaceous-Paleogene granular phosphorites of Arabian-African provinces (articles by V. I. Pokryshkin et al.). Difference in the component composition of phosphatic granular material in Arabian-African and central Kyzylkum granular phosphorites is expressed only in the quantity of the ratio of distinct organic remnants (biomorpha) and "grains."

The presence of diverse phosphatized organic remnants in microgranular (and aphanitic) phosphorites of Karatau, Dzhardzhina, Skalistii mountains, Khubsugul, and Altai-Sayan is noted by the numerous investigators studying them. Among them occur radiolaria, sponges, diatoms, brachiopods, pteropods, ostracods, chiolites, cephalopods, conodonts, foraminifera, crinoids, coprolites, "coprogenic formations," worm burrows, etc. Calcareous algae appear in phosphorites: Collenia in China (Sinan region) and Oncolites in Karatau [6]. Phosphatic formations with signs of organogenic occurrence were observed by the author in thin sections of phosphorites from Karatau (Dzhanatas, Aksai) and Khubsugul;* the structure of several phosphorites from the Khubsugul, Tsagannur, and Ukhagol occurrences strongly suggests the algae Epiphiton [18], while structures resembling algae also occurred in phosphates of both "twigs" and the space between them.

Differences which consist mainly of organic remnants are distinguished in phosphorites from various regions of the world. Thus, in Karatau, P. L. Bezrukov [3] described "organogenic phosphorites" with an abundance of elongated grains, spheres, and rods, which represent the phosphatized remnants of algae and some other kinds of microorganisms, while A. M. Tushina, again in Karatau, described organomorphic phosphorites, composed from fragments of phosphatic shells [29]. G. I. Bushinskii [7] cited layers of phosphorites significantly enriched in phosphatized organic remnants.

Various phosphatized organic remnants in phosphorites from different regions of the world were thoroughly illuminated by G. I. Bushinskii [6] and A. I. Smirnov [23]. They give descriptions of individual uncommon forms of phosphatic formations. Thus, L. P. Bezrukov detected unusual "mushroom-shaped" phosphorites which occurred on the mountain Dzhetym-Tal (Karatau). They are composed of cylindrical concretions which are oriented perpendicular to the layering planes, and are included in the regular phosphorite layers. The diameter of the concretions is 0.5-1.5 cm, the height reaches 4-5 cm, and they are distinguished on the layer surface with the form of prominences with concentric-conchoidal structure [3]. The author calls them a special variety, intermediate between layered and concretionary phosphorites. V. P. Maslov [18] finds similar forms characteristic for some algae, as well as for stromatoporoids. G. I. Bushinskii [6] distinguished a "lenticular-layered" type of phosphorite in the Sinan region: layers of phosphorite with thickness generally of 0.4-0.7 mm, sometimes up to 15 cm, while their extent in transverse sections varies from 3 cm to 3 m, and probably more. The layer thickness is generally constant and only sharply decreases in sloping areas. The layers are apparently sheetlike concretions

*Collection of the Central Asian experimental-systematic party (Branch of VNIIGOLNERUD, Tashkent).

which resemble pancakes. They are irregular in plan, and range in area from several centimeters to many meters, with perforations. G. I. Bushinskii proposed that these are "sheet-like concretions". V. P. Maslov found that similar morphological structures may be formed by individual forms of zoo- and phytoorganisms, for example several algae, Hydra polyps, stromatoporoids, etc. There are also other examples of similar descriptions. It is thus, probably, that phosphatized organic structures or their parts are described.

Oolitic varieties occur amid the granular phosphorites of Central Kyzylkum in which the nuclei of the phosphatic oolites are completely phosphatized shells of foraminifera; the structure of these phosphorites is perfectly analogous to the structure of the Karatau oolitic varieties. It is not excluded that the nuclei of the Karatau oolites may contain organic remnants. This was noted earlier for some of them [3, 29].

At the present time, basic geological rules for the arrangement of granular and microgranular phosphorites are established [10]: the stratigraphic, tectonic, lithological, paleogeographic, and geochemical rules, from which it follows that the conditions for the formation of the given phosphorite types have much in common. In particular, it is established that deposits of granular and microgranular (and aphanitic) phosphorites are correlated to shallow water parts (shelves), which appear at the present time and in the past as the zones of highest biological productivity [18].

It is known [10 etc.] that close paragenesis of granular, microgranular (and aphanitic) phosphorites with carbonates and siliceous rocks occurs: that phosphoritic layers, interlayers, and lenses are included amid carbonate and siliceous rocks, and that they contain carbonate and silica in various quantities and morphological forms. The following may be distinguished with reference to the Central Kyzylkum granular phosphorites: clay-carbonate rocks with carbonate components of organic origin, i.e., foraminiferal-nannoplanktonic marls, predominate amid the surrounding granular phosphoritic rocks; 60-80% of all of the phosphatic components contain principally phosphatized shells of foraminifera, which along with nannoplankton, are the rock forming organisms of the surrounding rocks.

The connection between the phosphatized organisms (diatoms, foraminifera) present in the various phosphatic components (concretions, grains, clusters, nodules, coprolites) and the rocks surrounding them (diatoms, foraminifera and foraminiferal-nannoplanktonic muds), is noted in phosphorites of Recent, upper Quaternary, and possibly pre-Quaternary age on the shelves of South West Africa and Chile-Peru [2].

An organic origin is established for many occurrences of microgranular (and aphanitic) phosphorites in siliceous rocks (Karatau, Phosphoria, China, etc.). There is rather a lot of data on the organogenic origin of the phosphatic bearing series, regarding carbonate rocks of the phosphorite bearing series. In the sequence of dolomites from the phosphorite bearing series of Karatau, beginning with the Malokaroisk suite and ending with the Krovli phosphorite bearing suite, N. G. Brodskiy and V. N. Kholodov [5] detected algae; among them algae reminiscent of Girvanella or Gummasolen altus Semikh, as well as numerous and diverse colonies of stromatolite in the form of branched columns (Linella), cupolas, loaf-shaped with fine concentric structures, etc. Abundant oncolites occur, and sometimes chiolites of Hiolithellus and Orthothella types. This data permitted the authors to draw a conclusion of a primary-biogenic (reefogenic) origin for the rocks of the sequence. In the article the authors cite the investigation of S. D. Levin, Yu. V. Mirtov and others, noting the correlation of phosphorites to zones where stromatolites and reefogenic limestones are developed in different regions of the country. G. I. Spanderashvili [27] noted the close connection of the phosphorites from Gorna Shoriya with algal dolomites. The phosphorites of the Sinan region represent the dolomite facies [6]. Cambrian-Riphean phosphorite bearing suites of Siberia also abound in algal remnants [11]. Fragments of phosphorites composed of the phosphatized blue-green algae Palaemic rosystis cf kairasensis [1] were found in lenses of Precambrian dolomites in the Kokpatas mountains (Central Kyzylkum).

From this it is possible to infer that probably all carbonate rocks of the phosphorous series from various phosphorite bearing basins have an organic origin, on which there is not yet always data or the traces of which are hidden by recrystallization. It might be otherwise said, that phosphorites are formed and are distributed amid rocks which require intensive organic life for their formation, and in the cases of Central Kyzylkum and shelf phosphorites, the above noted connection between rock forming organisms of the surrounding phosphoritic rock layers and the phosphatic components of the phosphorites is quite probable.

An exceptionally great number of proposals and assertions on the origin of one or another morphostructural varieties of phosphatic formation by means of phosphatization of various phyto- and zoogenic organisms is expressed at the present time in numerous articles both domestic and foreign by geologists studying phosphates. We will list some of them. Thus, we read in G. I. Bushinskii [6]: "In 1911, Breger thought that phosphatic 'grains' were formed by means of phosphatization of foraminifera or bacterial colonies, rolled along the bottom" (p. 32). American geologist G. D. Emi, studying phosphorites of the Phosphoria, drew the conclusion "that all pellets and even oolites represent phosphatized initially calcitic organic remnants." G. I. Bushinskii, E. R. Kressman, and R. V. Svanson thought pellets of Phosphoria (ovules, grains) were phosphatized coprolites of shallow water life; this idea was expressed as long ago as 1912 by Ya. V. Samoilov. Study materials of the granular phosphorites from Central Kyzylkum also entirely uniquely favor of a conclusion on the origin of phosphatic components by means of phosphatization of organic remnants.

The connection of phosphorites with algae was cited above. Varieties of morphological forms evolved by algae often correlate rather well with forms of phosphate in some phosphorites. Algae form [19, 20]: networks, nodules, outgrowths, crusts, accumulating on one another or stratifying in club shapes, concretions in the form of mounds, threads, clubs of threads, layers, standing stalks, and jointed bunches. Ropy algae form layer deposits. They envelop unevenness of the bottom or objects projecting from it (biohermal projections) with simultaneous securing of these objects into one whole. Crimson algae form mound and crustal forms, and nodules; nodules are sometimes formed by spiralling of thread around some fragment; sometimes some united cells in the overall slime create a colony in the form of a sphere, ellipsoid, etc. Stromatolites form thin (1 mm and less) layering. Many oncolites and nodules have oolitic structure, some have a characteristic angular or elongate form, others are composed from some bubbles of regular circular form, etc. [12]. In thin sections of microgranular and aphanitic phosphorites from some occurrences of Karatau, Khubsugul, Tsagannur, Ukhagol, and others, phosphatic formations were observed that were analogous in structure to many of the above cited morphological varieties of algae (oolites, layers, nodules), oolite-like, angular, twiggy forms, etc.

In recent years various remnants of organisms have been detected (including microorganisms and Metazoa) in "blank" sequences, and (as a result of oceanological investigations) an organogenic origin has been discovered for many carbonate and silica rocks of various age - from very ancient to Recent; the boundary of organic life at the present time has shifted to 4.25 billion years [26], that is, phosphorites, even the most ancient, were formed not only not in lifeless waters, but waters abundant in life.

Considering the thickness of carbonate rocks and the duration of time of phosphorite formation in ancient phosphorites, it is possible to assume that life in ancient waters proceeded extremely intensively, that carbonate- and silica-accumulation was prolonged, and that innumerable generations of organisms alternated and interchanged.

The foregoing makes the following conclusions possible:

- 1) Phosphatic components, that is, the forms of individual phosphatic material, in granular and microgranular (and aphanitic) phosphorites are in fundamental principle phosphatized organic remnants and products of their life activity.

- 2) The forms and sizes of individual phosphatic materials (morphostructural differences) are determined by the morphology of the phosphatized organic remnants: shells, folds, nuclei, small tubes (of worms), individual elements of algae, algal structures or their parts, etc.

- 3) These organic remnants are characterized by extreme variety, but in temporal intervals and in defined areas rock forming forms of organisms are the most distributed in correlation with the biological evolution of life on Earth and distributed biocoenoses. Algae seldom dominate in phosphorites of Riphean-Vendian age, since not one of stratigraphic classifications of the Precambrian is characterized so by such a vast distribution of various rock forming stromatolites and microphytolites as is the Riphean [26]. Later, numerous other siliceous and calcareous phyto- and zoorganisms acquired wide distribution.

Since various examples of the organic remnants listed above are present in the phosphorites of the different age intervals cited above: from the simplest organisms (algae, foraminifera) to organisms of a higher degree of evolutionary development, then couldn't bacteria (microorganisms), located on a much narrower stage of development, also exist?

Due to the absence of skeletal formations and their microscopic sizes they have been objects which have evaded observation for a long time, and they are presently little studied.

The existence of bacteria and microorganisms in connection with phosphorite formation has been proposed by many investigators [8, 9, 17, 24, etc.]. In a generalized form, their conclusions are: the processes of phosphate formation are connected with bacterial activity; structures of microbiogenic characteristics and corpuscles of coccobacillic form are observed in some phosphorites (Karatau); phosphate clumpets and grains may be products of the life activity of microorganisms or their corpuscles, replaced by phosphate; groups of microorganisms exist which are able to precipitate phosphate inside cells or in intercellular liquid. G. I. Spanderashvili [27] thought that dendritic appearing forms of phosphatic material, reminiscent of chains built up by cells of bacteria, to some degree indicates microbiogenic characteristics in phosphorites from Gorna Shoriya. In the opinions of different investigators, oolites may also be products of life activity of bacteria [29].

4) The phosphatized coprolites of both ancient invertebrates (known and possibly non-preserved nonskeletal) and later also vertebrate animals have a significant distribution in phosphorites. The concept that the quantity and mass of the coprolites often exceed the organisms that produce them, if one considers the latter's length of life, has not once been expressed by different authors. Their abundance attests to the continuity and intensity of life activity.

5) The process of replacement of organic remnants and the products of their life activity by phosphate in a medium of increased phosphorus concentration had the greatest value in the formation of phosphatic components (the question of a phosphorus source is not examined).

It is not excluded that a definite role belongs to components immediately inherent to the organisms: their secretory, enzymal, and hormonal materials, in the process of phosphatization. It is also not possible to exclude the contribution of microorganisms, moreover since they have lately become an established fact in the formation process of some minerals and mineral associations (sulfur, manganese hydroxides, bog iron ore, bauxites, jarosite; as a result of oceanological investigations - iron sulfides, etc.).

6) Mainly the skeletal parts of organisms underwent phosphatization. It is shown by the "soft tissues," the gelatinous corpuscles, bacterial cells, and algal slimes, that possibly two processes took place here: a) the formation of phosphatic material in media, corresponding to volumes of decomposed gelatins (with preservation of their organic components) and b) their immediate replacement. A. I. Smirnov [23] pointed out the replacement of "soft tissues" of organisms.

Thus, an excess of phosphorus entering a basin (or its zone) is manifest in two processes: in the development of a zone of high biological productivity and in the phosphatization of the components of its organisms after their death (decomposition).

7) It is possible to consider the community of organogenic remnants in phosphorites as respective temporal and territorial biocoenoses.

8) "Unrecognizability" (uncertainty) of biomorphic formation of phosphatic components is caused by the following factors: a) disintegration (breakdown, erosion, creeping, etc.) of the sediment in which the phosphatization occurred at various stages of its lithification; b) hydrodynamic activity (rounding, concentration, dispersion); c) diagenetic and catagenic transformations, recrystallization of phosphatic material: from weak micropolarization to formation of microgranular crystals of apatite or their aggregates, etc.; d) reactional interrelations of phosphate with the cementing material; e) the degree of phosphate replacement: from initial to complete, etc. The factors cited above probably appear in different degrees, from very weak to significant.

One of the causes of the "unrecognizability" of the origin of phosphatic components as due to the replacement of organisms by phosphate, in particular some algae, may be deficiencies in the study of phosphorites, particularly in ancient ones, in standard thin sections, (as well as in study of algal rocks). Due to randomness of the slices in thin sections, a significant quantity of phosphatic formations of various forms look circular, oval or elongate, that is, oval "grains." Thus, for study of the Central Kyzylkum phosphorites, synthetic thin sections were prepared from various well preserved biomorphozoa that were specially selected under binocular; in the sections, the greater part appeared to be "grains" of the above described forms.

Thus, phosphorites are an impression of life in sediments. In 1929 Ya. V. Samoilov had already called them biolites.

LITERATURE CITED

1. M. A. Akhmedzhanov and É. R. Bazarbaev, "New data on the age of the Kokpatassk suite of Bukantau (Central Kyzylkums)," *Uzb. Geol. Zh.*, No. 5, 82 (1967).
2. G. N. Baturin, *Phosphorites on the Ocean Floors* [in Russian], Nauka, Moscow (1978).
3. P. L. Bezrukov, "Geological structure of the Karatau phosphorite bearing basin and the basic results of geologic exploratory efforts," in: *Phosphorites of Karatau* [in Russian], Izd. Akad. Nauka KazSSR, Alma Ata (1948), pp. 3-66.
4. V. S. Boiko, N. V. Shabanina, and V. Ya. Il'yashenko, "Petrographic characteristics of granular phosphorites of Central Asia," in: *Material Composition of Phosphorites* [in Russian], Nedra, Novosibirsk (1974), pp. 158-164.
5. N. G. Brodskaya and V. N. Kholodov, "On the possibility of reefogenic occurrence of dolomites in the phosphorite bearing sequence of Malyi Karatau," *Dokl. Akad. Nauk SSSR*, 165, No. 6, 1365-1368 (1965).
6. G. I. Bushinskii, *Ancient Phosphorites of Asia and Their Genesis* [in Russian], Nauka, Moscow (1966).
7. G. I. Bushinskii, *Phosphorite Formation* [in Russian], Nauka, Moscow (1969).
8. A. G. Bologdin, "On one little studied, but important group of mineral organisms," *Dokl. Akad. Nauk SSSR*, 49, No. 9, 698-701 (1945).
9. A. G. Bologdin, "Geologic activity of microorganisms," *Izv. Akad. Nauk SSSR, Ser. Geol.* No. 3, 19-38 (1947).
10. *Geology of Phosphorite Occurrences, Methods for their Prediction and Exploration* [in Russian], Nauka, Moscow (1980).
11. E. A. Eganov, *Geosynclinal Phosphorites of Siberia and the Far East* [in Russian], Nauka, Moscow (1968).
12. Z. A. Zhuravleva, "Distribution of oncolites in reefogenic deposits of the southern Urals," *Izv. Akad. Nauk SSSR, Ser. Geol.*, No. 2, 38-55 (1980).
13. Sh. Zhuraev, "On the formation of phosphatic grains in Alaisk deposits in the southwestern extensions of the Gissarsk ridge," *Dokl. Akad. Nauk UzSSR*, No. 1, 40-42 (1970).
14. N. Ibaidullaev, "On new types of phosphoritic manifestations in Paleogene deposits of Kyzylkums," *Uzb. Geol. Zh.*, No. 3, 24-29 (1968).
15. N. Ibaidullaev, "Material compositions and genesis of phosphorites in the Paleogene Kyzylkums," *Uzb. Geol. Zh.*, No. 6, 59-61 (1972).
16. V. Ya. Il'yashenko, "Industrial-genetic classification of phosphorite occurrences from the central part of Central Asia," *Uzb. Geol. Zh.*, No. 1, 78-83 (1980).
17. N. G. Kassin, "Phosphorites of north of the Vyatsk province," *Bull. Geokomite*, No. 5, 13-18 (1925).
18. V. P. Maslov, *Atlas of Rock Forming Organisms* [in Russian], Nauka, Moscow (1973).
19. V. P. Maslov, *Stromatolites* [in Russian], Izd. Akad. Nauk SSSR, Moscow (1960).
20. V. P. Maslov, *Fossil Calcareous Algae of the USSR* [in Russian], Izd. Akad. Nauk SSSR, Moscow (1956).
21. V. I. Pokryshkin, V. S. Boiko, and V. Ya. Il'yashenko, "Regularities in the distribution of granular phosphorites from the Arabian-African provinces and Central Asia," *Litol. Polezn. Iskop.*, No. 6, 102-119 (1978).
22. V. S. Popov, "Characteristic features of granular phosphorites from the Kyzylkumsk basin," *Uzb. Geol. Zh.*, No. 6, 52-59 (1981).
23. A. I. Smirnov, *Material Composition and Conditions for the Formation of Basic Types of Phosphorites* [in Russian], Nedra, Moscow (1972).
24. V. A. Sokolov and I. I. Mashkara, "On the microstructure and genesis of the Karatau phosphorites," *Probl. Sov. Geol.*, No. 7, 90-93 (1938).
25. S. I. Sokolov, G. Fatkhullaev, and N. Ibaidullaev, "Paleogene granular phosphorites of the Central Kyzylkums," in: *Genetic Types and Estimates of Prospects of Nonore Mineral Resources in Central Asia* [in Russian], SAIGIMS, Tashkent (1977), pp. 22-37.
26. B. S. Sokolov, "The organic world of the earth on the path to Phanerozoic differentiation," *Vestn. Akad. Nauk SSSR*, No. 1, 126-143 (1976).
27. G. I. Spanderashvili, "Phosphorites of Gorna Shoriya," in: *Phosphorites of Western Siberia* [in Russian], Nedra, Moscow (1965), pp. 14-56.
28. N. V. Shabanina, V. S. Boiko, and Yu. P. Zhuravlev, "Results of the petrographic study of middle Eocene granular phosphorites from Central Kyzylkum," *Uzb. Geol. Zh.*, No. 4, 76-78 (1982).

29. A. M. Tushina, "On phosphatic oolites and spherulites in the Karatau phosphorites," *Zap. Vsesoyuz. Mineral. O-va.*, **89**, No. 1, 46-51 (1960).
30. M. Égamberdyev, "New phosphoritic horizons in upper Cretaceous and Paleogene sedimentary formations of the Auminzatau mountains (Kyzylkum)," *Graduate student articles, Department of Technical and Geological-Chemical Sciences*, No. 1, Tashkent, *Izd. Akad. Nauk UzSSR* (1958), pp. 153-164.

GEOLOGIC RELATIONSHIPS OF STRATIFORM LEAD-ZINC METALLIZATION
AND OIL-PRODUCING STRATA (WITH SPECIAL REFERENCE TO THE SOUTH
VERKHUYAN AREA)

D. I. Pavlov and A. L. Galyamov

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With special reference to the South Verkhoyan area, the space-time relationships of stratiform lead-zinc metallization and oil-producing strata are described. It is shown that the genesis of the ore-forming solutions of this type of metallization cannot be interpreted correctly without studying its catagenetic component. The significance of this component determines the geologic conjugation of the processes responsible for the development of stratiform lead-zinc and oil deposits.

In [11, 16-19, 26, 27] the metallogenic role of catagenetic ore-producing systems has been described; it is particularly noticeable in margins of oil and gas basins. Metallization of this kind is typically localized in such margins [21] where long-term pulsational discharge of thermal solutions is concentrated; these solutions are generated at hypsometrically deeper levels and convey dissolved organic matter and metals. Under certain hydrodynamic, geochemical, and other conditions, these, originally catagenetic (thermodehydrational) and sedimentogenic solutions, could have been conducive to oil accumulation; as a result, the processes forming oil and ore deposits in sedimentary beds of oil and gas basins were conjugated geologically.

In this paper we discuss the space and time correlations of a stratiform lead-zinc metallization in the South Verkhoyan area with oil-producing formations. The principal metallization of the region (Sardana, Urui, and Pereval'noe deposits) and its numerous ore shows are localized in the dolomitized carbonate Vendian of the Maya-Kyllakh structural-formational zone, situated at the juncture of the Siberian platform and the Verkhoyan-Kolyma folded region (Fig. 1).

Primary (i.e., not redeposited and less recrystallized) ores are substantially spherulitic; the data of numerous investigators indicate that they were formed during sedimentary processes. A redistribution of ores accompanied by an increase in the relative proportion of galena occurred at temperatures of 200-380°C [24]. The underlying horizons display numerous ore shows; the more promising indications are localized in the Upper Riphean beds of the Lakhandia series.

The main oil-producing beds in the section of sedimentary basins are known to be clay formations [2]. High-pressure catagenetic solutions are formed in them mainly as a result of hydromicatization of montmorillonite. The depth interval where such generation is especially intense is included in the main oil formation zone, described by Vassoevich. Usually, on the basis of Burst's theory [18], it is limited to temperatures of 85-120°C; for an average geothermic gradient (3°C/100 m) this corresponds to a depth of 3-4 km. The

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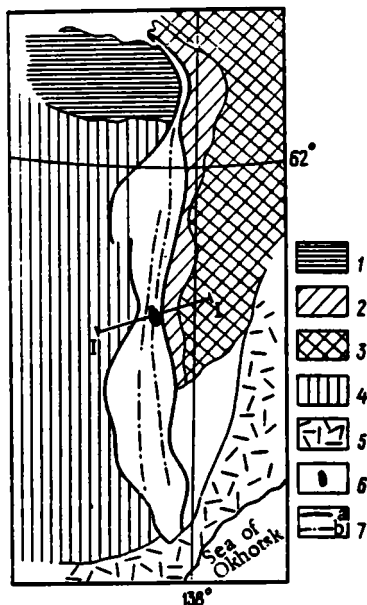


Fig. 1. Position of the Maya-Kyllakh structural-formational zone (white) amid the principal tectonic elements of the southeastern margin of the Siberian platform: 1) Verkhoyan trough; 2) Sette-Daban rise; 3) South Verkhoyan synclinorium; 4) Siberian platform; 5) Okhotsk-Chukotskii volcanic belt; 6) principal metallization area; 7) regional faults (a) and tectonic disruption zones (b); I-I = positions of model schemes (see Fig. 3).

geological time required by a formation to pass through this interval is long; it is approximately equal to the time of compensation of the basin floor subsidence to at least 1 km.

Primary clay formations are prominent among the Riphean of the South Verkhoyan area (Fig. 2). Terrigenous sections of the Kerpyl and Lakhandia series are believed to be the main oil-producing strata [12]. Heightened concentrations of bitumoids of an oil genesis (and much less often, liquid oil drops) are observed at the various levels of the Riphean section; some of them are syngenetic to the enclosing rocks, while others have migrated from greater depths. They are distributed according to a certain regularity among the levels of the section (see Fig. 2): as the basin subsided, the newly lowered clay intervals were brought into a setting of the principal oil formation zone.

Geological correlation of the stratiform lead-zinc metallization of the South Verkhoyan area and the potential oil-producing beds should be supported by the finds of solid naphthides and carbon gases, as well as oil-producing beds in this region. In addition, the mineral composition of ores (pyrite, sphalerite, galena, dolomite, calcite, quartz, glauconite, etc.) is virtually identical to that of neomorphs in collector formations of the region [12], confirming the affinity of the underlying generative processes.

The geologic history of the South Verkhoyan area was largely determined by the interrelationships of its three constituent tectonic entities: the Maya-Kyllakh zone of near-fault folding, the Sette-Daban folded-block rise, and the South Verkhoyan synclinorium. During the Riphean they all evolved in a similar fashion, resulting in slow (at most 0.1 mm/year [8]) accumulation of the same sedimentary formations on the platform and its subsided eastern side.

We will examine the further evolution of the South Verkhoyan area in terms of model schemes that consider the possible position of an interval of maximum thermodehydration, corresponding in first approximation to the principal oil-formation zone in the section of this region. The schemes describe the situation at the beginning and end of the Vendian and the end of the Early Carboniferous and the Middle Jurassic (Fig. 3). In all the schemes the interval is hatched; the background geothermic gradient is assumed nominally to be 3°C/100 m and during volcanic activity 10°C/100 m.

The first scheme (see Fig. 3a) shows that, under our assumptions, the Middle Riphean deposits by the beginning of the Vendian in the western part of the territory were in conditions conducive to thermodehydration processes; at the same time, in the eastern part of the territory the Upper Riphean sediments were in that interval. The Lakhandia series of the Upper Riphean was in an intermediate position, which largely coincided with the boundaries of the Maya-Kyllakh zone. The complete strata were brought into this setting by the beginning of the Vendian.

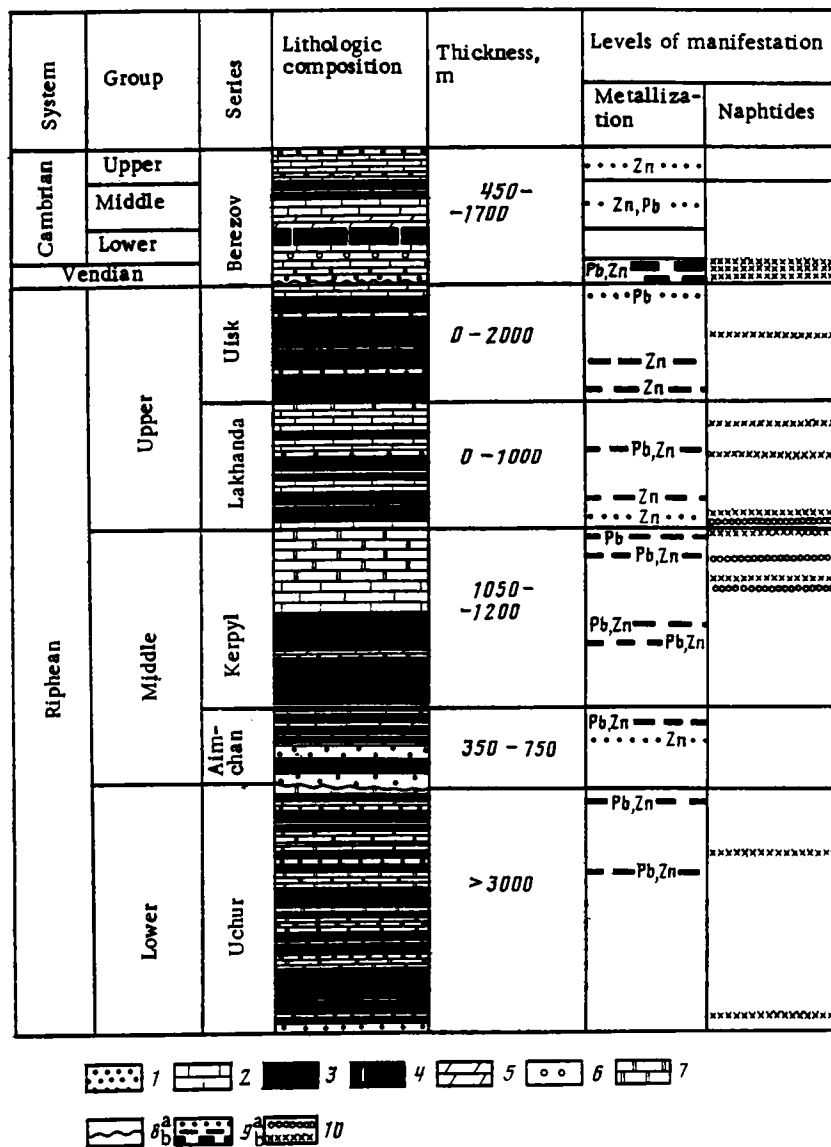


Fig. 2. Generalized section of the Riphean-Cambrian sediments in the Maya-Kyllakh zone and the positions of the signs of stratiform lead-zinc mineralization and naphtides (data from [3, 12] and data of A. V. Korobitsyn have been used in this compilation): 1) sandstone; 2) limestone; 3) argillite siltstone; 4) bituminous schist; 5) marlstone; 6) glauconitic limestone, locally lyddites; 7) dolomites; 8) disconformities; 9) stratiform lead-zinc metallization (a - mineralization points, b - signs, c - deposits); 10) signs of naphtides (a - fluid, b - solid).

During the latter half of the Vendian and the early Cambrian, the Sette-Daban and South Verkhoyan synclinoria experienced volcanic activity. The rise of the geothermic gradient was local; accordingly, the scheme for the end of the Vendian (see Fig. 3b) presents both the strata subjected to volcanic heating and those that were free of this influence. The elevated level of thermal energy intensified the generation of solutions in the Upper Riphean. Some of the deep levels were locally heated to more than 400°C.

A map has been compiled in order to identify the portions of the region's Riphean beds that favored the generation of catagenetic solutions during the Vendian. The map combines: a) the composite isopachytes of the maximum thickness of the Early and Middle Riphean (i.e., Uisk, Lakhandia, Kerpyl, and Aimchan series) and b) isopachytes of the deposits of the Uisk

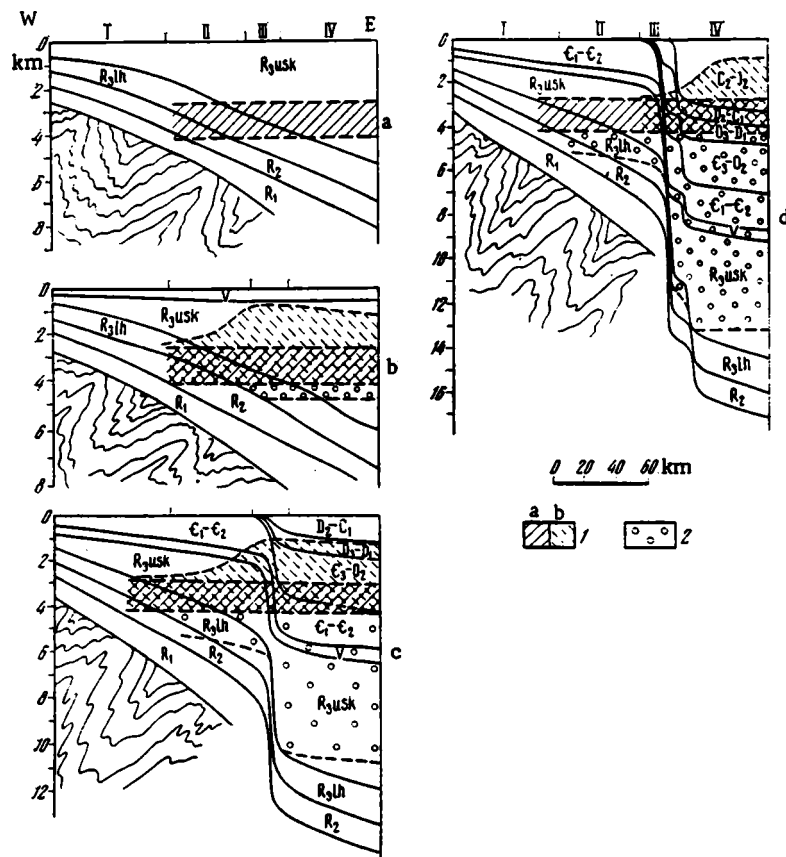


Fig. 3. Model schemes of thermal dehydration of sediments in the South Verkhoyan area: (a) Early Vendian; (b) Late Vendian; (c) at the end of the Early Carboniferous; (d) at the end of the Middle Jurassic; (1) sediments subjected to thermal dehydration (a - in absence of volcanic activity; b - with volcanic activity); (2) sediments after thermal dehydration at 3°C/100 m (since the beginning of the Vendian). Regions: (I) Siberian platform; (II) Maya-Kyllakh zone; (III) Sette-Daban; (IV) South Verkhoyan synclinorium.

series of the Upper Riphean, with special indication of the areas where the composite thickness of these strata was greater than 2500, 3000, and 3500 m. Combining these numbers with the thickness of the upper part of the Lakhanda series of the Upper Riphean, which was virtually free of terrigenous deposits and occurred under the Uisk series (Salar suite), we obtain at least 2800, 3300, and 3800 m. Thus, for the geothermic gradient 3°C/100 m the terrigenous Lakhanda sediments by the time when the development of the Uisk series was completed was brought into conditions favoring thermodehydration processes. There is a distinct area of maximum subsidence, where the thickness of Uisk sediments exceeds 3500 m, i.e., terrigenous sediments of the bottom of the Uisk series, as well as the Lakhanda series, were brought into an environment that favored catagenetic generation of thermal solutions.

The map identifies the area where the total thickness of the Uisk sediments was 2000-2500 m. Like the northwestern parts of all subsided territories, it stretches in the northwesterly direction, which is emphasized by the local deep on the Belaya River (Khando) along the same course. During the Vendian this territory included a local rise, stretching to the northwest; the deposit and the numerous ore shows of Sardan are confined to this rise [24].

Of the two locations where the Uisk sediments exceed 3000 m, only the northern part belonged to the maximum subsidence area throughout the Middle-Late Riphean rather than just the Uisk time (see Fig. 4). The composite thickness of these sediments is greater than 65 m. The northern area is particularly favorable for long and multiple generation of catagenetic solutions and gases by the subsiding Riphean strata.

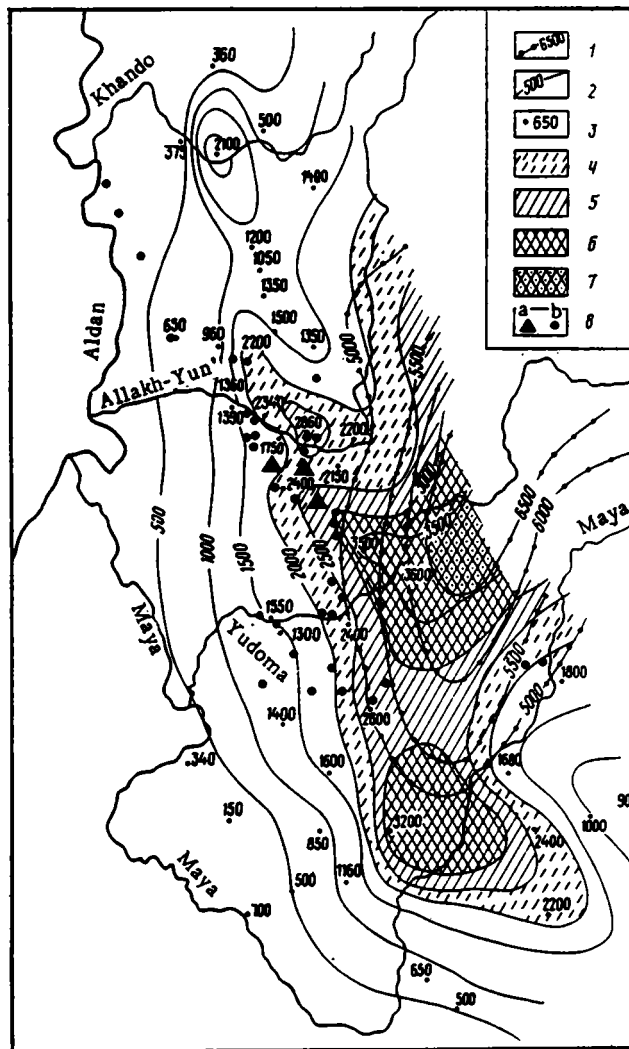


Fig. 4. Schematic map comparing the thicknesses of the Middle-Upper Riphean of the South Verkhoyan area and the distribution of stratiform lead-zinc deposits and ore signs (Vendian level) based on data of Davydov [24], the Yakutian Geological Agency, and the Aerial Geology Agency: (1-2) isopachytes (1 - maximum total thickness of Middle-Upper Riphean, 2 - thickness of Uisk series Upper Riphean); (3) locations of the Uisk group sections and their thickness; (4-7) areas of Uisk sediments thickness, m (4 - 2000-2500, 5 - 2500-3000, 6 - 3000-3500, 7 - >3500); (8) stratiform lead-zinc sediments (a) and ore shows (b).

The main metallization and most ore indications have a tendency to occur along the margins of the maximum subsidence area. The highest pressure gradients of waters released from the Middle to Upper Riphean were directed toward the main metallization sites. As mentioned before, the spatial distribution of metallization was also affected by the north-western course of the structures that began to develop during the Late Riphean [4, 5]. The ore finds (see Fig. 4, top), relatively remote from maximum subsidence areas, are distinguished from the other ores by a peculiar isotopic composition of lead in galena.

During the Early Paleozoic, the Maya-Kyllakh zone stabilized after becoming attached to the platform that was no longer subsiding. Sediments accumulated at a rate which sometimes (the Early Ordovician) was as high as 0.15 mm/yr; the process continued only in more eastern parts: the Sette-Daban and South Verkhoyan synclinorium. The transverse section of the region exhibits the first flexure bend, corresponding to the boundary between the Maya-Kyllakh zone and Sette-Daban (see Fig. 3c). Sometimes the sagging (especially during the Middle Devonian-Early Carboniferous) was associated with volcanic activity. The general appearance of Sette-Daban and the South Verkhoyan synclinorium during that time

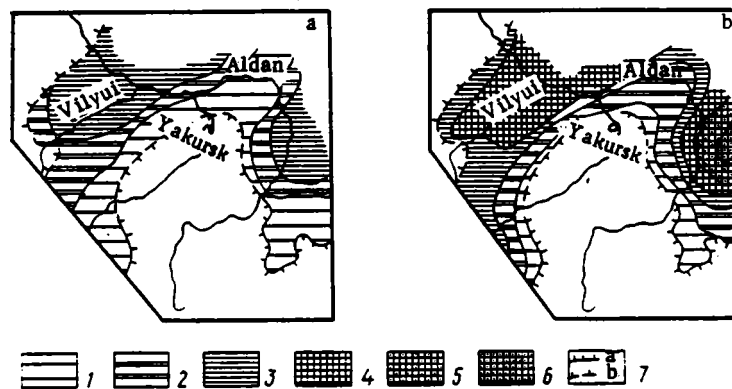


Fig. 5. Distribution of the densities of residual (a) and original (b) organic matter in the Riphean of the southeastern perimeter of the Siberian platform (copied from schematic map compiled by Larichev [9]): (1-6) density of organic matter, million tons/km² [1) 1-2; 2) 2-5; 3) 5-15; 4) 15-50; 5) 50-100; 6) >100]; (7) boundary of modern occurrence of Riphean sediments (a - proven, b - hypothetical).

resembled a rift [10]. By the end of the Early Carboniferous pronounced thermodehydration conditions encompassed the Ordovician; where volcanic heating was added, the Lower Devonian was also engaged. Starting from the Middle Devonian - when the anhydrite strata were formed at Sette-Daban [6] - sedimentogenic brines with a salt content of up to 200 g/kg could be present in permeable strata [1].

The foundation time of the second flexure, corresponding to the separation of Sette-Daban and South Verkhoyan synclinorium, was the end of the Early Carboniferous, when Sette-Daban stabilized. After that time, the general sagging continued only in the South Verkhoyan synclinorium, where thick terrigenous formations of the Verkhoyan complex continued to accumulate through the Middle Mesozoic (see Fig. 3d). During the Late Triassic the accumulation rate was 0.23 mm/yr [8].

According to geophysical investigations, the total thickness of sediments in the lowest-subsided parts of the South Verkhoyan synclinorium is approximately 18 km. According to geologic data, the total thickness of the Riphean-Paleozoic strata alone was almost 30 km already at Sette-Daban [29]. In a discussion of the causes of this large discrepancy, Korostelev [8] calls attention to the migration in time and space of the axes of the maximum subsidence and sedimentation zones. Against the general background of prolonged sagging and the inherited sediment accumulation in South Verkhoyan troughs (which were interpreted by Korostelev as geosynclines), these axes and zones migrated eastward, which was true not only for the trough but for its constituent smaller structures as well. During the initial development stage of each such structure, the maximum subsidence zones were near their western borders, but later were shifted into the center; starting with the inversion motions, the next migration of the maximum sagging of troughs in the easterly direction took place.

Stavtsev has proved that during the Vendian-Aldanian, Middle Paleozoic, and especially Middle Mesozoic, the South Verkhoyan territory was subjected to tectonic stresses that increased from west to east and were realized in the unidirectional and inherited evolution of the modern structural plan [23].

Tectonic stresses and the increased heat flow intensified the dehydration of sediments at all depth levels of the newly evolved troughs. The consistent step pattern of the consolidation of South Verkhoyan, the large thickness of sediments accumulated in the earth's interior, and the association with several sedimentary cycles with terrigenous beds at the base can be regarded as important factors indicating not only the duration but the repeated generation of catagenetic solutions - up to the completion of the sagging process at the basin floor during the Middle Jurassic. A considerable thickness of strata is one of the factors responsible for the development of high-temperature fluids released from the deep sediments during epochs of tectonic activation.

Regardless of the origin of solutions and gases released from sediments (simple expression, thermodehydration, and further premetamorphic and metamorphic "regeneration"), their pressure gradients and lateral displacements during all stages of the region's history were directed mainly westward, toward the previously consolidated and least-subsided Maya-Kyllakh zone. The total amount of fluids including the hydrocarbon fluids, which also migrate from the depths of the adjacent troughs towards the margins of platforms, is proportional to the length of migration and regional ancient gradients [22]. According to these characteristics, based on [14], the conditions were most favorable for such migration on the territories of the Cis-Baikal and Aldan-Maya troughs. The length of migration has been estimated at 460 and 400 million years for regional ancient grades of 29 and 24 m/km. By comparison, these quantities have been estimated for the Vilyui hemisyncline at 135 million years (end of the Early Permian-beginning of the Early Cretaceous) and 18 m/km, representing the generation power of this megastructure known for its commercial oil and gas prospects, as being much smaller than similar processes in the above-mentioned troughs.

Remarkably, the principal metallization is not only confined to the perimeter of the maximum sagging regions and the areas of maximum ancient regional slopes (see Fig. 4), but also to the narrowest cross section of the Maya-Kyllakh ore-bearing zone (see Fig. 1). This was the location where throughout its history tectonic impulses from discharge of predominantly horizontal stresses of the earth's crust must have been most contrastive [23], especially in view of the "rigid stop" provided at the side of the platform by the Khamnin rise.

In this context, it is possible to correlate consistently the geologic environments of the formation of rising gas and water solutions and the stratiform lead-zinc metallization of the South Verkhoyan area. Their characteristic feature is the rise of the temperature (and, accordingly, the role of the gas phase in the fluids) in the course of the development of these solutions and the fact that it continued for a long time. The general picture also resolves the apparent contradiction between the Vendian age of the "primary" (sedimentary-diagenetic) metallization and the Middle Paleozoic model age of the lead ore. Isotopic data are interpreted as resulting from a mix of the lead separated at different geologic times (Vendian-Jurassic) from the sinking sediments. The lead in the deposits, as opposed to the region as a whole and the places of ore signs, displays a narrow range of isotopic values. The homogeneity is probably due to the multiple redeposition of mineral matter, determined by mineralogical observations, which resulted in a leveling of the isotopic compensation. The model age of lead in the ore shows that are the farthest from the subsided part of the region (see Fig. 4, top) is much younger than in the other formations of the Vendian in the area (up to an age of 10 million years for galena of the Sakharin ore show). Since there are no Upper Riphean sediments, including Lakhanda (the Vendian occurs here on the Middle Riphean), this has been interpreted as resulting from a minor presence of the "ancient" component in the orelead and the relatively greater importance of the "young" component [20]. If that is so, the very presence of the latter can be interpreted as an indirect confirmation of the significance of early ores (the sedimentary-diagenetic entities) among the deposits; these ores were redeposited repeatedly, which determined the resulting Middle Paleozoic model age of lead in them.

The multiplicity of ore formation processes was also observed in the history of the development of deposits in time and in space. The evolution of the deposits (and the history of metallization) was determined by three tectonic stages. During the first of these stages, gentle folds were formed which make up the synsedimentary positive structure of a northwesterly course, mentioned earlier. The second and third stages were the periods of formation of steep meridional folds of the Recent structural plan associated with intense fissuring and redistribution of metalliferous components [5].

To gain a better perspective we will estimate the loss of metals and scattered organic matter by the deeply subsided Riphean strata of the region (organic matter could have participated in the transport of metals).

Petrographic observations indicate that the Riphean sandstones in the area consist of "drained" varieties, from which mafic components and much of the feldspars were washed out, while the quartz in them was repeatedly generated. Postsedimentary alteration in these rocks must have resulted in a substantial removal of metals. More than 500 complete chemical analyses of the principal types of Riphean rocks from ore-free sections have been interpreted with calculations on a Mir-2 computer, indicating that these rocks are sharply

depleted of metals as compared with the Clarke levels. The mean gross contents of lead, zinc, and copper in the Riphean clay rocks of the Maya-Kyllakh zone were often lower than even their generally lower total Clarke level for carbonate rocks (0.33×10^{-2} wt%). In the carbonate rocks of the same sections they are far lower than this value (for example, in dolomites at the top of the Tsipanda suite of the Middle Riphean the values amount to 0.1-0.2 wt%). The levels of a relatively higher content of the same metals (5×10^{-2} - 13.5×10^{-2} wt%) are associated with higher iron contents (more than 45 wt% recalculated to trivalent iron), especially with interlayers of siderite ores. Such interlayers occur in the Riphean section alongside sulfide layers. The section appears as an alternation of layers enriched in and depleted of metals. The contrastivity of metal distribution in the folded parts of the region has been shown to be much higher than in the platform areas; the redeposition of metals from deeper layers to the shallower levels is related to the intensity of the geotectonic setting. When it became more intensive (or when the heat flow was intensified), the rocks were dehydrated more and more metals were washed out, both from clays and collector rocks, as released water percolated into them [20]. An approximate estimate of the volumes of catagenic solutions and zinc migrated with them (given in [19]) suggests that these volumes along (not counting sedimentary water) were sufficient to build up a major metallization.

Larichev [9] constructed schemes to summarize information on initial and residual amounts of dispersed organic matter in potentially oil-producing Riphean strata of the region; these data can be used to estimate the amount of loss of scattered organics (Fig. 5). According to a conservative estimate that disregards the maximum densities of the initial organics in the South Verkhoyan synclinorium that were in excess of 100 million tons/km², the removal of organic matter from the Riphean constituted 45-85 million tons/km². In absence of favorable geologic premises for localization of oil and gas deposits, this immense, highly reactive mass should have been realized in some other forms.

The influence of the structural and tectonic factors is felt also in the distribution of bitumoids, in particular, their substantial compositional and concentrational fluctuations in lithologically and stratigraphically homogeneous complexes. An analysis of bitumen distribution in the Riphean confirmed that substantial amounts of solutions migrated in this section repeatedly [20].

It is beyond doubt that the amount of metals and organics extracted from Riphean strata that underwent catagenetic alterations is, as such, comparable to the metallization scale and the amounts of agents necessary to transport metals (under the assumption that chloride transport only became possible from the Middle Devonian, when halogenesis evolved at Sette-Daban).

In conclusion, we will note the possible oil and gas prospects of the region associated with producing strata younger than the Riphean.

The geologic relationships described in this paper suggest that the Maya-Kyllakh zone during the long Paleozoic-Mesozoic evolution of the South Verkhoyan area drained a stream of fluids generated at depths in the Sette-Daban and South Verkhoyan synclinorium that continued to sink to greater depths. The Vendian and the Cambrian, with high organic contents (particularly the domanikoid Inikan suite of the Lower Cambrian), stand here to depths sufficient for them to realize their oil-generating powers. By draining the flow of catagenetic fluids, the Maya-Kyllakh zone essentially functioned as an anticonservational zone of an oil and gas basin [15, 17] that possibly was formed to the east of it. As a result, particularly in the transitional areas between South Verkhoyan synclinorium and Sette-Daban and from Sette-Daban to the Maya-Kyllakh zone, hydrocarbon deposits, including those of the "underoverthrust" type, may have been formed.

The high accumulation rates of these sediments, associated with heightened thermal flux density allow classifying the South Verkhoyan synclinorium (according to Sokolov [22]), especially during the Mesozoic, as a highly active source of oil and gas formation, in the category characterized by a predominance of oil placers over gas deposits.

Studies by Cherskii et al. [28], who described the role of tectonoseismic factors in the formation and accumulation of hydrocarbons, suggest that the optimal premises for the development of major oil and gas accumulation zones exist in so-called heterogenic basins combining two structural elements: an active element adjacent to the folded zone and a passive (platformal) element. A prolonged and intense generation of hydrocarbons and

the filling of the oil and gas accumulation zones is promoted by an early stabilization of the passive zones, while the active zones continue to evolve for a long time, up to the present. As has been shown earlier, this is the combination observed in the geologic history of the South Verkhoyan area during the Phanerozoic (see Fig. 3), which makes this region similar to the less studied Cis-Verkhoyan area, compared by Cherskii with the largest heterogeneous basins outside the USSR (in the Near and Middle East, Western Canada and Orinoco).

The good prospects of heterogeneous basins are derived from the fact that, while retaining the direction of pressure gradients from active to passive zones and the lateral migration of fluids during their catagenetic generation, ever new producing strata became involved in the process as they continued to sink to greater depths. In addition, in the interior of even strongly tectonically disrupted troughs relatively calm areas are usually preserved, which, retain for very long geologic periods of time, fluids that existed at various stages of extrusion and unloading [25]. Any further extrusion of these fluids could cause a new manifestation of seismotectonic activity, which holds true for Recent generation of catagenetic metalliferous solutions and hydrocarbons in the ancient strata that have not yet completed their catagenetic alteration. Lomtev [13] suggested that this is precisely the condition of the Riphean of the subsided eastern margin of the Siberian platform (the Maya-Aldan depression), where hydrocarbon generation processes took place recently or continue even today.

* * *

The data reported in the present paper indicate that the development of the principal (Vendian) ore-bearing strata of the South Verkhoyan area and the generation of catagenetic metalliferous solutions by the oil-producing beds of the Lakhanda series of the Upper Riphean coincided in time. The discharge of these fluids was controlled by tectonically weakened zones and synsedimentary rises conjugated with them [7]; these rises were located mainly within the ore-bearing zone. There is a distinct spatial tendency of metallization to be confined to such rises [5], situation on the near perimeter of maximum subsidence locations in the region where the largest amounts of catagenetic solutions were formed. All this is evidence that the genesis of metalliferous solutions of the stratiform lead-zinc metallization of the Vendian in the South Verkhoyan area cannot be interpreted correctly without an analysis of the catagenetic ingredient of such solutions. By acknowledging the definitive role of this ingredient we can not only interpret the formation of stratiform lead-zinc and oil deposits as geologically conjugated processes controlled by the evolution of the sedimentary basins [19], but also study the multistory pattern typical for these groups of deposits and covering large stratigraphic intervals and resulting from the multistory pattern of clay beds that evolved gradually during the sinking of the basins.

LITERATURE CITED

1. E. A. Baskov, Foundations of Paleohydrogeology of Ore Deposits [in Russian], Nedra, Leningrad (1983).
2. N. B. Vassoevich, Yu. K. Burlin, A. I. Konyukhov, and E. E. Karnyushina, "The role of clays in oil and gas formation," Sov. Geol., No. 3, 15-29 (1975).
3. I. G. Volkodav, A. I. Gorbunov, and V. F. Mekhonishin, "Prospects for developing of a new polymetal base in Yakutia," Razvedka Okhrana Nedr, No. 10, 6-10 (1976).
4. A. L. Galyamov, "The influence of folding on the distribution of lead and zinc ores in carbonate rocks of the Yudom-Maya rise (southeastern Yakutia)," in: Structural Control of Hydrothermal Metallization in Stratified Formations [in Russian], Nauka, Moscow (1986), pp. 41-50.
5. Yu. V. Davydov, A. L. Galymov, M. L. Mel'tser, and A. G. Chiryaev, "Ore-controlling factors and forecasts of ore bodies in stratiform lead and zinc deposits of southeastern Yakutia," Geol. Geofiz., No. 1, 101-107, (1982).
6. A. A. Ivanov and Yu. F. Levitskii, Geology of Halogenous Deposits (Formations) of the USSR [in Russian], Gosgeoltekhizdat, Moscow (1960).
7. A. A. Kartsev, "Hydrogeological conditions of oil and gas accumulation," Izv. Akad. Nauk SSSR, Ser. Geol., No. 10, 115-121, (1979).
8. V. I. Korostelev, Geology and Tectonics of the South Verkhoyan Region [in Russian], Nauka, Novosibirsk (1982).
9. A. I. Larichev, "Accumulation conditions and distribution of organic matter in the

- Riphean in the Siberian Platform," in: New Data on Geology and Oil Prospects of the Lena-Tunguska Province [in Russian], SNIIGGIMS, Novosibirsk (1982), pp. 96-111.
10. K. K. Levashov, "Paleorift structure of the eastern margin of the Siberian platform," *Sov. Geol.*, No. 10, 59-75 (1977).
 11. A. V. Lipaeva and D. I. Lavrov, "Groundwater and iron ore formation in the northern Aral area," *Litol. Polezn. Iskop.*, No. 2, 104-117 (1986).
 12. S. G. Sarkisyan (ed.), *Lithology and Oil Gas Prospects of the Southeastern Siberian Platform (the Upper Precambrian)* [in Russian], Nauka, Moscow (1980).
 13. V. A. Lomtev, "Oil and gas prospects of the southeastern Siberian platform," in: *Formation and Distribution Patterns of Oil and Gas Deposits* [in Russian], IGIRGI, Moscow (1974), pp. 108-113.
 14. K. I. Mikulenko and G. S. Fradkin, "Tectonic criteria of oil and gas in marginal depressions of the Siberian Platform," in: *Oil and Gas Prospects of the Upper Precambrian Phanerozoic of the Eastern Siberian Platform* [in Russian], YaF SO AN SSSR, Yakutsk (1986), pp. 4-17.
 15. V. B. Olenin, *Oil Geology Zoning Based on Genetic Principles* [in Russian], Nedra, Moscow (1977).
 16. D. I. Pavlov and E. S. Postel'nikov, "The source of ore material in the Angara-Pitsk basin of sedimentary iron ores," *Litol. Polezn. Iskop.*, No. 6, 3-22 (1980).
 17. D. I. Pavlov, "Factors usually overlooked in studies of the contribution of groundwater to the development of a stratiform lead and zinc metallization," in: *Groundwater and Evolution of the Lithosphere (Proceedings of a National Conference)* [in Russian], Nauka, Moscow (1985), pp. 207-208.
 18. D. I. Pavlov, "Potentially oil-producing formations as sources of ore-forming solutions of a stratiform lead and zinc metallization in the southeastern margin of the Siberian platform (basic principles of research)," in: *Genesis of Rare Metal and Lead and Zinc Stratiform Deposits* [in Russian], Nauka, Moscow (1986), pp. 29-43.
 19. D. I. Pavlov, D. I. Gorzhevskii, and A. A. Kartsev, "Development of a stratiform lead and zinc mineralization as a result of evolution of sedimentary basins," in: *Stratiform Ore Deposits* [in Russian], Nauka, Moscow (1987), pp. 60-67.
 20. D. I. Pavlov, I. V. Chernyshev, and D. A. Khivtsov, "Lead and zinc stratiform deposits," in: *Endogenous Sources of Metalliferous Materials* [in Russian], Nauka, Moscow (1987), pp. 199-212.
 21. V. V. Popov, *Geological Environments of Exogenous Hydrothermal Ore Formation* [in Russian], Nedra, Moscow (1980).
 22. B. A. Sokolov, *Evolutionary and Dynamic Criteria for Evaluation of Oil and Gas Prospects of Deep Layers* [in Russian], Nedra, Moscow (1985).
 23. A. L. Stavtsev, *Tectonics and Mineral Resources of Conjugation Zones of Ancient Platforms and Mobile Belts* [in Russian], Nedra, Moscow (1983).
 24. V. A. Kuznetsov and A. L. Yashin (eds.), *Stratiform Lead and Zinc Deposits in the Vendian of Southeastern Yakutia* [in Russian], Nauka, Novosibirsk (1979).
 25. A. E. Khod'kov, "Groundwater dynamics of compacting marine sedimentary strata and their structure-forming role," *Izv. Akad. Nauk SSSR, Ser. Geol.*, No. 12, 85-94 (1962).
 26. V. N. Kholodov, *Postsedimentary alteration of elisional basins* [in Russian], Nauka, Moscow (1983).
 27. V. N. Kholodov, "Role of regional catagenesis in the formation of thermal gas-water solutions (a contribution to the theory of stratiform metallization)," in: *Genesis of Rare Metal and Lead and Zinc Stratiform Deposits* [in Russian], Nauka, Moscow (1986), pp. 6-28.
 28. N. V. Cherskii, V. P. Tsarev, T. I. Soroko, and O. L. Kuznetsov, *Influence of Tectonic and Seismic Processes on Hydrocarbon Development and Accumulation* [in Russian], Nauka, Novosibirsk (1985).
 29. V. A. Yan-Zhin Shin, *Tectonics of the Sette-Daban Horst-Anticlinorium* [in Russian], YaF SO AN SSSR, Yakutsk (1983).

This paper discusses the spread, the formation environment, and the evolution of carbonaceous, terrigenous, and terrigenous-carbonate sediments in the Riphean of the Bashkirian meganticlinorium. Types of carbonaceous sediments of various origins are identified and described. Their role in the stratotypic section of the Riphean in the western slope of South Ural is shown to decline progressively from the Burzyan series to the Karatau series.

Carbonaceous strata have been studied recently with renewed vigor, largely due to their paragenetic association with vanadium, gold, copper, iron, uranium, fossil fuels, and other deposits [13, 14]. Although in the past few years carbon-containing strata were studied intensely in the Precambrian carbonaceous beds, reconstruction and classification of their formation environments and analysis of the metallogenic specialization of strata enriched in organic matter (OM) still remains to be completed [13]. The terrigenous-carbonate complexes of the stratotypic Riphean section of the Bashkirian meganticlinorium in South Ural are the favorable objects of such studies, because carbonaceous beds in them occur at several stratigraphic levels. The main objective of our research was to reconstruct the environments of their formation and identify the types of carbon-containing beds so as to be able to study the data on geochemistry and metallogenic specialization of these sediments and predict the metalliferous prospects of these strata on the basis of lithologic-formational analyses.

In the section of the "ancient strata" of the Bashkirian meganticlinorium the carbonaceous complexes occur mainly at the bottom of the Burzyan series, which is comprised of the Aisk, Satkin, and Bakal suites and their analogs in the central part of the territory - the Bol'sheinzersk, Suran, and Yushin suites [15] (Fig. 1). Investigators distinguish Kisezan, Satkin (Suran), and Bakal (Yushin) development levels of carbonaceous sediments. The Burzyan series in the northern parts of the meganticlinorium began to be deposited at the time of foundation of rift or graben structures, which were probably connected with aulacogens of the eastern margin of the Russian platform [2]. The active tectonic conditions of the early Aisk time, the block motions of the basement, and the related contrastive topography were conducive to the development of diverse facies and accumulation of coarse clastic poorly sorted sand-gravel-pebble, gravel-sand, and sand-silt-clay deluvial-proluvial and alluvial-deltaic sediments of the Navyshk, Lipov, and Chudinsk subsuites of the Aisk suite. Trachybasaltic volcanites found amid the Navyshk rocks were formed in subaerial and shallow-water settings and, according to Parnachev [9, 10], are indicative of the time when the rift structures were founded. In the sections of the Navyshk subsuite, terrigenous rocks are represented by conglomerates, gritstone, inequigranular sandstone, and variegated argillite. They were probably accumulated at the beginning of the transgression in littoral cliff settings, when the incipient basin protruded as tongues into the mountainous landmass, compounded by tectonic ledges or valleys, and pebblestone development zones could coexist at short distances with portions of volcanic effusions, proluvial fans, and small deltas. This is illustrated clearly by the sections of the Navyshk subsuite near Arshinka Village, to the southwest of Tra-Tash Mountain, and the western piedmont of Greater Miass Mountain, where effusive formations alternate with poorly sorted boulder-pebble sediments, and the sand-gravel sediments exhibit features suggesting that they were formed in alluvial flood plains and probably deltaic environments (a regular decrease in the thickness of the oblique series and the granulometric composition of rocks in isolated obliquely stratified members from top to bottom, the unidirectional oblique stratification with a rhythmic sorting of material, desiccation cracks in the fine-grained flood plain sediments, etc.).

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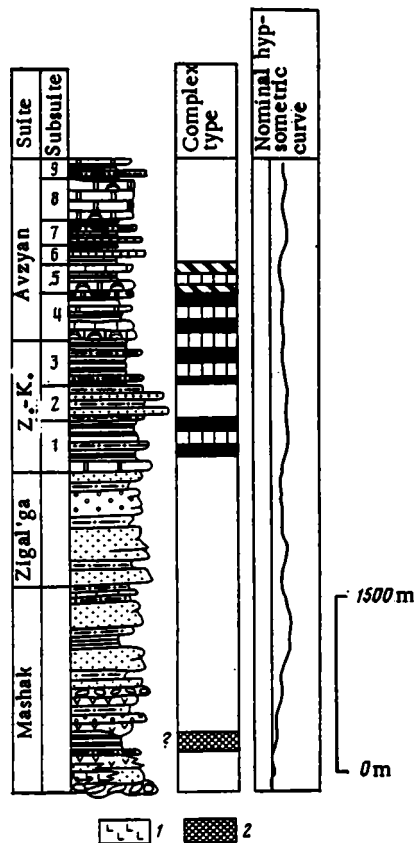


Fig. 2. Occurrence levels and types of carbonaceous sediments in the section of the Middle Riphean of the Bashkirian meganticlinorium: 1) acid effusives; 2) carbonaceous sediments, presumably associated with volcanites. Other notations as in Fig. 1. Numbers in the columns specify subsuites (strata): 1) Ambar; 2) Seregin; 3) Tukan; 4) Kataskin; 5) Maloinzersk; 6) Ushakov; 7) Kutkur; 8) Revet; 9) Tyul'men. Z. K.) Zigazin-Komarov.

The section of the Aisk suite is crowned by Kisezan and Sungur subsuites. These consist of a thick monotonic bed (up to 700-900 m) of black and dark-grey coaly-clay schists and phyllites with rare interlayers of horizontally stratified siltstone. They constitute the first level of carbonaceous sediments in the Riphean of the Bashkirian meganticlinorium. The schists display fine or medium tabellarity and even bedding surfaces. The layering is usually indistinct, but sometimes fine horizontal or striated discontinuous stratification is underscored by the alternation of unevenly thick black and gray interlayers. The dark layers are on average 3-6 mm thick; the lighter layers, 1-2 mm thick. Their boundaries are distinct. The dark (black) layers are of a similar color; the lighter ones usually have a thin horizontal striation. Small pyrite cubes often occur in schists.

These data suggest that the Aisk time was the foundation period of contrastive tectonic structures with exceptionally uneven sinking of the seafloor portions. The contrastive relief and the active tectonic processes helped intense erosion of coarse-grained clastics, which accumulated in the littoral strip of the basin. Sedimentation was compensated or overcompensated, and the latter half of the Aisk time was marked by an excessive deepening of parts of the basin, creating favorable conditions for the formation of thick strata of fine-grained terrigenous ooze enriched in OM; they accumulated in relatively deep and calm settings.

During the Satkin time the further transgression increased the aquatorium, and the accumulation of terrigenous deep-sea ooze was replaced by formation of chemogenic and phyto-genic carbonates. The top and middle Satkin suite include the Polovinkin and Karagai sub-levels of carbonaceous beds. The former consists mainly of black and dark-gray sericite-quartz-clayey schist and clayey-coaly phyllitelike schist with subordinate rare interlayers of gray siltstone and marly dolomite. The schists display a fine interstratification of dark coaly clay and thin layers enriched in quartzose silty matter. The boundaries of the layers are sharp and clear. Presumably, by the middle Satkin time the transgression in the northern part of the Bashkirian meganticlinorium reached a maximum, and the carbonaceous fine-grained terrigenous sediments were formed in the central part of the shallow epicontinental basin. There was a limited influx of silt and psammitic clastics, which had a pulsational pattern. This fine stratification is typical for many black schist strata of the Late Precambrian [7] and is probably determined by the specific type of the basin with fine-

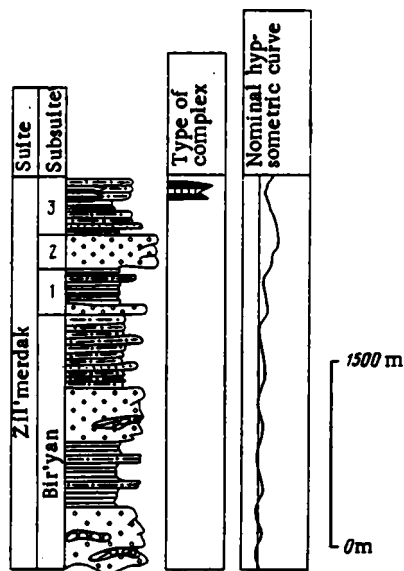


Fig. 3. Position of carbonaceous sediments in the section of the Upper Riphean (Zil'merdak suite) of the Bashkirian meganticlinorium. Notations as in Figs. 1 and 2. Numbers in the columns specify subsuites: 1) Nugush; 2) Lemezín; 3) Bederyshín.

grained high-organic terrigenous sediments accumulation. Characteristically, OM is confined to the sediments at the center of the basin; this has been noted by Strakhov [16] as a global regularity.

The latter half of the Satkin time witnessed a shallowing of the basin and accumulation of chemogenic carbonate sediments unevenly enriched in terrigenous material. The Karagai sublevel of carbonaceous rocks confined to the upper Satkin subsuite consists of dark-gray almost black coaly-clay dolomites and flat-detrital carbonate breccias with interlayers of coaly-clay and coaly-carbonate-clay schists. The latter vary in thickness from 7-10 cm to 2.5 m and more. The C_{org} content in the black schists varies from 0.34 to 1.36%. Generally, the schists are not stratified but consist of thin plates. There are also oxidized pyrite crystals. The coaly matter in the schists, according to Anfimov [3], is represented by finely dispersed graphite scattered through the rock or grouped in thin veinlets. The beds and members of dolomites exhibit alternating dark-gray and black strips, ranging from 0.5 to 4 cm in thickness. The black strips are of a homogeneous appearance, while the light strips consist of thin parallel layers. The rocks include numerous interlayers and lenses of light coarse-grained dolomite from 1-2 to 12-15 cm, which are distributed conformally to the layering. Segregations of oxidized pyrite are sometimes confined to them.

The Bakal level comprises at the bottom a thick monotonous bed of horizontally stratified coal-sericite clay schists of the Makarov subsuite; at the top it displays alternating members of mafic carbonaceous schists and chemogenic carbonates (limestone, dolomite, and dolomitic limestone). C_{org} content in Makarov schists is 0.4-0.5%; in the schists of the upper Bakal subsuite it varies from 0.26 to 0.5%. A lithologic-facies study of the Bakal suite [2, 8] has shown that terrigenous and carbonate sediments at the end of the Early Riphean in the northern part of the Bashkirian meganticlinorium were formed in an environment of shallow near-shore basins, remote zones, and lagoon coasts. The frequent change of carbonate and terrigenous sedimentation regimes at the end of the Bakal time and an increased influx of terrigenous clastics during the accumulation time of carbonate sediments seem to indicate unstable tectonic conditions and an incipient gradual regression of the basin.

In the central and southern parts of the meganticlinorium, carbonaceous strata in the Early Riphean accumulated mainly in shallow-sea environments. They are typical for the Berdagulov and Serdauk sublevels (Suran suite) and the Yushin level, corresponding to the sediments of the Yushin suite. Dark coaly-clay, often silty schists associate in the sections of this zone with small-grained sandstones and siltstones that bear traces of their shallow-sea genesis (small oblique stratification, gentle wavy interlayering of various lithologic rock types, etc.), dolomites, and limestones, forming complex interstratified members or homogeneous members that are tens of meters thick. The Early Riphean complex in this territory was formed in a relatively calm tectonic environment. Initially (the Bol'sheinzersk time), these were apparently the deep-sea parts of the basin, where most

clastics were supplied by periodic gravity flows. Later, the basin grew shallow, and shallow-sea sediments were accumulated mainly during the Suran-Yushin time. The only exception was the coaly-clay schists of the Serdauk subsuite of the Suran suite, which were apparently formed in more distant, open-sea zones.

During the Early Riphean, the northern and central parts of the Bashkirian meganticlinorium probably developed in different environments. In the north, one distinguishes clearly a transgressive (relatively shortlived but active) stage, a stage of maximum expansion of the sea aquatorium (inundational), and then a period of gradual basin contraction. In the central and southern parts of this structure, shallow-sea settings prevail almost throughout the Early Riphean. This was probably due to the fact that the northern sedimentation zones were connected more closely with aulacogens of the eastern Russian platform margin, and all geologic events there were more active and contrastive. The northern regions in the contrastive bathymetry of the basin were the more probable locations of the development of smaller stable accumulation zones of high-organic fine-grained sediments, whereas further south the development of carbonaceous sediments in shallow settings was accompanied by a depletion of clastic and chemogenic carbonate material.

The accumulation of carbon-containing sediment in the Middle Riphean was preceded also by a period of active basic and acid volcanism (Mashak volcanogenic-sedimentary complex) and formation of thick conglomerate-sand beds (Fig. 2). Unlike the earlier Riphean stages, the carbonaceous sediments in the Mashak suite are almost unknown (except for its third Bykov bed [12], where coaly-silty-clayey schists form members of up to 100 m). The first level of carbonaceous sediments in the Middle Riphean appeared only after the accumulation of a thick (sometimes up to 700-800 m) complex of extraquartzose sandstones of the Zigal'ga suite; their formation was related to the participation of mature products of chemical weathering in sedimentation processes and occurred during stabilization of tectonic and paleogeographic conditions in an extensive shelf-type basin. The structural specifics of the Zigal'ga sandstones indicate that sandy sediments of current and wave zones, slope sediments, and other shallow-sea units accumulated mainly in the basin in that period. Against this background, conditions were created sporadically for the deposition of thin members of coaly-clay-silt sediments, associated with the periodically drying parts of shoals.

In the post-Zigal'ga section of the Middle Riphean in the Bashkirian meganticlinorium two distinct levels can be identified in carbonaceous sediments. The first level corresponds to the Seregin and Tukan subsuites of the Zigazin-Komarov suite; it is represented by dark-gray and black quartz-sericite-clay and coal-sericite-clay phyllitelike schists alternating with siltstone and small-grained quartzitelike sandstone. This horizontal or gentle wavy stratification is discernible in sandstone and siltstone. Sculptures of desiccation cracks are sometimes present in the lower bedding surfaces of sand-silt rocks. Peculiar members of "wormlike rhythmites" are found in the sections of the Seregin subsuite near Bakal, on the eastern slope of the Bazal ridge, and in other locations; these are coal-clay schists with interlayers or lenses of gray siltstone, up to 2-5 cm thick and with intensely disrupted internal structure. Besides horizontal siltstone interlayers, numerous bent, branching, or swollen and often crossing veinlets are observed which branch off horizontally to interlayers up and down. Thicker layers (up to 3-5 cm) project bent siltstone veinlets only down, and in a perpendicular cross section resemble desiccation cracks. The fact that the members adjacent to "wormlike rhythmites" also exhibit desiccation cracks on the sandstone and siltstone layering surfaces suggests that "rhythmites" were formed from thin-layer packets of interstratified coal-clay and siltstone interlayers, which were previously disrupted by desiccation cracks and were then subjected to sand diapirism, as described by Kholodov [17]. Generally, the Seregin subsuite accumulated in a shallow-sea basin that periodically dried out. The Corg content at the bottom of this level in isolated samples attains 1.58%. In the second sublevel of carbonaceous sediments in the Zigazin-Komarov suite (as well as in the first sublevel), coaly-clay schists are interstratified with siltstone, fine-grained sandstone, and rare dolomite interlayers. The set of sediments of the Tukan subsuite was apparently formed in a shallow marine basin.

The second level of carbonaceous sediments consists of the Kataskin and Maloinzersk subsuites of the Avzyan suite. Dark high-organic clay schists form interlayers amid carbonate rocks or are included in terrigenous interstratification members. Generally, they are of a limited importance. Lithologic and structural features of rocks indicate that sediments accumulated in a shallow sea.

Carbonaceous sediments are less widespread in the Upper Riphean terrigenous-carbonate complex as compared with the other Riphean subdivisions described earlier (Fig. 3). They are observed only in the southern sections of the Zil'merdak suite, where they are associated with littoral-marine sediments of the early transgression period. Beds of black clay, massive dolomites, or dolomites with fine washed-out structures or oblique wavy stratification are observed along the Kuzha and Greater Nugush rivers, upstream of Galiakberovo in the middle of the Berderyshin subsuite of the Zil'merdak suite. They alternate with members of interstratified fine-grained dark-gray sandstones, siltstones, and dark (almost black) silty schists. The latter are up to 10 cm (sometimes 50 cm) thick. Small sculptures from desiccation cracks are often seen on the lower bedding surfaces of sand-silt layers; the layers themselves include angular schist platelets, suggesting that the sediment accumulated in locations where subaquatic and subaerial sedimentation environments replaced one another in an alternating succession.

An analysis of the evolution of sedimentation settings of carbon-containing beds in the Riphean of the Bashkirian meganticlinorium suggests the following. During the Early Riphean carbonaceous sediments were confined to the phase of rapid transgression, accumulated during maximum transgression and stabilization periods, and also during gradual contraction of the area of the shallow marine basin. The Lower Riphean carbonaceous terrigenous sediments tend to associate mainly with the middle of the sedimentary cycle. In the Middle Riphean "black schists" were formed after the transgression epoch, as they did during the Early Riphean. However, if in the Early Riphean this was directly connected with the active development of the basin, the carbonaceous sediments of the Zigazin-Komarov and Avzyan levels accumulated after a long period of stabilization of paleogeographic and paleotectonic environments. The role of the black schist complexes in the Middle Riphean is noticeably reduced. Usually, these are diverse interstratification members of a shallow-sea genesis, where the black carbonaceous schists are not the predominant lithologic type. Black terrigenous strata with a high content of organic matter are generally not typical for the Late Riphean. Instead, we see variegated carbonate and terrigenous sediments of a continental shallow-sea and marine origin. The massive development of glauconite is an indicator of normal marine sedimentation environments.

The available data allow identifying three types of carbonaceous complexes in the Riphean section of the Bashkirian meganticlinorium. The first complex consists of thick (up to several hundred meters) beds of marine coal-clay carbonate-free schists, which give way, up the section, to shallow-marine carbonate and terrigenous formations. They correlate with the end of the Aisk, the middle of the Satkin, and the beginning of the Bakal times. The second type apparently includes members of dark coal-clay schists (from several meters to fractions of a meter thick), occurring in an association with carbonate (chemogenic, phytogenic, and clastic) rocks and terrigenous rocks of a shallow-sea origin, observed in the upper Bakal sublevel and Suran, Yushin, Zigazin-Komarov, and Avzyan levels. The third complex includes coal-clay-carbonate shallow-sea sediments of the Satkin suite top, and, probably, several members in the Kataskin subsuite of the Avzyan suite.

Carbonaceous rock sets are widespread in Upper Cambrian sections [13]. For example, Bazhenova et al. [4] identified in Siberian Riphean sections more than 15 stratigraphic levels, variously enriched in OM. The formation epochs of carbonaceous sediments were largely confined to transgressive (less often regressive) stages of major sedimentation cycles; by contrast, sediments of this kind are virtually unknown in Siberia in the stages of maximum transgression. The facies accumulation settings of carbonaceous sediments along the perimeter of the Siberian platform varied from lagoonal to littoral-marine to normal-marine. Bazhenova and co-workers have discovered an empiric regularity: most carbonaceous beds were formed after the accumulation of the variegated and red complexes, regardless of the stage in the sedimentary cycle. Unlike the Siberian sections, the Riphean of the Bashkirian meganticlinorium has its black schist beds associated with transgression epochs and, mainly, maximum development stages of shallow epicontinental sea basins.

The Riphean carbonaceous rocks of several regions of the folded surroundings of the Siberian platform include sulfur pyrite, sulfur pyrite-polymetallic, polymetallic, manganese, iron and other ores [7, 11]. Although until recently it was impossible to establish any distinct correlation between Corg contents and heightened concentrations of trace elements in coal-clay schists [1], the fact that ore concentrations can be found in black schists is remarkable in and of itself, because carbonaceous complexes are considered by many investigators to be a probable source of oil components [13]. Even within favorable

carbonaceous complexes, however, metallization is controlled by structural and other factors [5], which is essential for exploration planning.

In conclusion, we will note the following priority aspects of studies of carbonaceous sediments of the Bashkirian meganticlinorium: further investigation and detailed description of the formation conditions of the sedimentary complexes identified in the paper; formational classification of these sediments on a genetic basis; and detailed interpretation of the correlations between these complexes and the types of sedimentation basins in the Riphean and their evolution stages. A thorough and purposive study of the geochemistry of coal-clay and coal-carbonate sediments is also indispensable; the objective should be to identify the levels of heightened regional concentrations of trace elements and to determine their correlations with Corg contents in rocks; in addition, metallogenic specialization of the complexes and the specific stratigraphic levels is recommended. The results could be combined to determine the promising levels and locations for detailed exploration and reconnaissance, thus "dovetailing" important practical needs with the objectives of regional descriptive studies.

LITERATURE CITED

1. E. P. Akul'shina, Yu. P. Kazanskii, V. G. Petrov, et al., "Carbonaceous sediments of the Upper Precambrian of Yenisei ridge: lithologic-geochemical characteristics and formation environments," in: Problems of Sedimentary Geology of the Precambrian, Issue 7, Part 2 [in Russian], Nauka, Moscow (1981), pp. 11-16.
2. L. V. Anfimov, "Carbonate lithogenesis and the related ore formation in the Lower Riphean of the Bakal-Satkin district in South Ural," in: Stratigraphy and Lithology of Precambrian and Early Paleozoic Sediments of the Ural [in Russian], UNTs Akad. Nauk SSSR, Sverdlovsk (1982), pp. 77-86.
3. L. V. Anfimov, V. D. Visygin, and L. E. Demina, Satkin Magnesite Deposit in South Ural [in Russian], Nauka, Moscow (1985).
4. T. K. Bazhenova, A. V. Ivanovskaya, Yu. I. Ipatov, et al., "Carbonaceous strata of the Upper Precambrian and the Lower Paleozoic of the Siberian platform: Lithology and geochemistry, formation conditions, and metallogenic characteristics," in: Problems of Sedimentary Geology of the Precambrian, Issue 7, Part 2 [in Russian], Nauka, Moscow (1981), pp. 96-101.
5. V. A. Buryak, "Genetic types of deposits in carbonaceous beds," in: Problems of Sedimentary Geology of the Precambrian, Issue 7, Part 2 [in Russian], Nauka, Moscow (1981), pp. 162-167.
6. M. I. Garan', "The western slope and the central zone of South Ural," in: Stratigraphy of the USSR [in Russian], Gosgeoltekhizdat, Moscow (1963), pp. 114-161.
7. E. M. Gribov and E. M. Gurvich, "Metalliferous carbonaceous formations of the Yenisei ridge," in: Problems of Sedimentary Geology of the Precambrian, Issue 7, Part 1 [in Russian], Nauka, Moscow (1981), pp. 173-181.
8. M. T. Krupenin, "Lithologic and facies composition of Bakal siderite formation," in: A. N. Zavaritskii Institute of Geology and Geophysics: A Yearbook, 1982 [in Russian], (1983), pp. 24-30.
9. V. P. Parnachev, "Late Precambrian volcanogenic-sedimentary complexes of the Bashkirian anticlinorium," in: Pre-Ordovician History of the Ural [in Russian], Ural Science Center, Academy of Sciences of the USSR, Sverdlovsk (1980), pp. 40-60.
10. V. P. Parnachev, "Formational classification of volcanogenic-sedimentary complexes of the Riphean in the Bashkirian meganticlinorium," in: The Precambrian of the Phanerozoic Folded Belts [in Russian], Nauka, Leningrad (1982), pp. 96-106.
11. V. G. Ponomarev, E. P. Akul'shina, and S. V. Saraev, "Carbonaceous carbonate-schist Precambrian strata and syngenetic pyrite-polymetallic metallization in the Yenisei ridge," in: Problems of Sedimentary Geology of the Precambrian, Issue 7, Part 1 [in Russian], Nauka, Moscow (1981), pp. 169-178.
12. A. F. Rotar', Z. M. Rotar', and V. P. Parnachev, "Stratigraphy of the Shatak suite, Middle Riphean, South Ural," Stratigraphy and Lithology of Precambrian and Early Paleozoic Sediments of the Ural [in Russian], Ural Science Center, Academy of Sciences of the USSR, Sverdlovsk (1982), pp. 53-65.
13. A. V. Sidorenko, Sv. A. Sidorenko, and N. A. Sozinov, "Carbonaceous formations of the Precambrian and their metalliferous characteristics," in: Problems of Sedimentary Geology of the Precambrian, Issue 7, Part 1 [in Russian], Nauka, Moscow (1981), pp. 9-17.

14. E. A. Sozinov and Sv. A. Sidorenko, "Terrigenous-carbonaceous Precambrian and Phanerozoic formations," in: Terrigenous Rocks of the Early Precambrian [in Russian], Kol. Fil. Akad. Nauk SSSR, Apatity (1977), pp. 39-52.
15. Riphean Stratotype, Stratigraphy, Geochronology (Transactions of the Geological Institute, Academy of Sciences of the USSR), No. 377, (1983).
16. N. M. Strakhov, Geochemistry of Recent Oceanic Lithogenesis [in Russian], Nauka, Moscow (1976).
17. V. N. Kholodov, "Sand diapirism: A new aspect of catagenetic processes: Paper 1," Litol. Polezn. Iskop., No. 4, 50-67 (1978).

THE ROLE OF HYDROGEOCHEMICAL ANOMALIES IN CATAGENIC PROCESSES DURING THE FORMATION OF OIL-GAS AND GAS-CONDENSATE DEPOSITS

V. N. Disler

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The catagenetic processes involved in the development of liquid and gaseous hydrocarbon accumulations are shown to be determined by the variable features of hydrogeochemical anomalies. The methods of chemical thermodynamics are used to estimate the limits of the alteration of clay minerals by the activity of condensation waters. The degree of kaolinization of clay cement by condensation waters under most favorable conditions is shown to never exceed single-digit percentages of the total amount of cement in rocks containing gas or oil-gas deposits.

Normal hydrochemical zonality develops during the formation history of a sedimentary basin. Hydrochemical anomalies develop within a relatively limited time range and are localized in space. Anomalous hydrochemical fields arise as a result of active tectonic processes, such as rising or sinking of formations, development and renovation of faults, magmatic and fluid intrusions, etc.

The waters of normal hydrochemical zones determine the alteration of rocks and, specifically, regional authigenic mineralization corresponding to the various lithogenetic stages according to the thermobaric and lithification characteristics. Hydrochemical anomalies are associated with their specific authigenic mineralization; on the other hand, the development of mineralogic anomalies presupposes the existence of specific hydrogeochemical conditions during the history of the sedimentary basin.

Sedimentary strata with oil, gas, and gas-condensate deposits are characterized by certain specific authigenic mineral associations. The mineral associations inside the deposit contours appear as anomalies against the background of the general mineralogic zonality. Studies of these anomalies, however, indicate significant differences in the evolution of the catagenetic processes. Numerous authors have noted the "retardation" of catagenesis within the contours of hydrocarbon accumulations [17, 20, 27]; other investigators, however, have described a clear catagenetic change [13]. There is also a theory that the processes of catagenesis never completely cease [10]. All these theories proceed from detailed mineralogic and geochemical studies and correlations of sections inside and outside of oil and gas accumulation contours.

Catagenetic processes slow down as oil and/or hydrocarbon gases are brought into the bed, because relative to the enclosing rocks these are nonpolar "inert" compounds. This interpretation was suggested in [27], with special reference to productive bed XVII of the Okobykai suite of the Miocene terrigenous strata of the northern Sakhalin, studied in the Kolendo, Ékhabi, Sabo, and other deposits. Bed XVII consists of quartz-feldspar graywackes

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with a polymineral clay cement (chlorite-kaolinite-hydromica-montmorillonite). The retardation of secondary processes was estimated by the alteration of feldspars and biotite, the crystallization degree of cement clay matter, and the preservation of accessory minerals, typically unstable to intralayer dissolution [27]. Within the contours of certain gas deposits, however, a higher degree of kaolinite crystallization to large flakes and aggregations has been described. Catagenetic processes outside the deposit contour continue to develop under the effect of formation waters of the normal hydrochemical zonality.

Activization of superimposed catagenesis during the formation of oil and gas deposits can be illustrated by sand-clay and silt strata in western Siberia, reported in [13]. The study determined that sand rocks were changed from lithoclasts in the Jurassic to neutral arkoses in the Lower Cretaceous and acid arkoses in the Upper Cretaceous. The composition of clay minerals changed from hydromica (Jurassic) to chlorite (Lower Cretaceous) and montmorillonite (Upper Cretaceous), while the kaolinite content fluctuated. Biotite content developed to a sharp maximum in the Lower Cretaceous. The regional pronounced catagenetic alterations of clay matter are hydromicatization of montmorillonite through a phase of mixed-layer montmorillonite-hydromicaceous formations. Abnormal halos of kaolinization of sand rocks was also noted. The degree of kaolinization was described as being stronger in locations where the terrigenous Mesozoic sediments are associated with the main oil and gas deposits and much less obvious near isolated placers. Similar effects have been described by various investigators for the oil and gas strata in many parts of the USSR [6, 12, 22, 23, 26]. In recent years marine drilling in the Sea of Okhotsk determined large-scale kaolinization within the contours of several oil and gas-condensate deposits. Lebedev et al. drew the following conclusion from these studies: "If our theory that epigenetic kaolinite is formed by superimposed processes is correct, kaolinization should be viewed as the obligatory phase in the development of oil and gas accumulations" [13, p. 70]. This interpretation can be viewed as opposite to the concept of "retardation" of catagenetic processes by the formation of oil and gas deposits.

In [13] it was noted that, besides kaolinization in commercial oil and gas beds of the Lower Cretaceous, catagenesis gives rise to a chlorite modification that differs from the contemporaneous analogs outside oil and gas contours. The authors of [13] concluded that the catagenetic alteration of chlorite, as it were, "prepares" it for kaolinization. Components such as Mg^{2+} , Ca^{2+} , SiO_2 , and Fe^{2+} are washed out and then redeposited as regeneration quartz, carbonate, etc. The development of kaolinite after clay cement in pores combined with regeneration quartz rims is generally a typical consequence of catagenetic processes often reported in publications on oil and gas provinces of the USSR.

If the "retardation" of catagenetic processes is based on the fact that oil is unpolarized and "conservative" with respect to catagenetic rock alteration, the instances where such alteration takes place should be confirmed by finds of some active agents capable of performing it. Several theories have been suggested to this effect.

In studying hydrogeochemical environments in the northern Sakhalin, the author became interested in the effect of hydrochemical inversion in the structures of several oil and gas deposits.

There have been numerous publications on the finds of inversional waters with a low salt content in oil and gas deposit areas [8, 18, 24, and others]. In the past few years investigators have increasingly attributed this phenomenon to the formation of so-called condensation or solution waters. Their peculiar composition and sharp differences from the normal formation waters, as well as the fact that they occur in previously known and newly discovered oil and gas provinces, call for evaluating the influence of these waters on catagenetic processes; it is the subject of the present paper.

Condensation waters have been studied for over two decades. A comprehensive discussion of their role in the hydrogeology and oil and gas deposits was undertaken in [7, 8]. Gritsenko [4] studied the formation of condensation waters experimentally. In a study of hydrocarbon systems containing water vapors he showed that when pressure is lowered isothermally, two liquid layers (condensate and water) rather than one layer (condensate) are released at formation temperature. Previously, Sultanov [24], proceeding from the data on water saturation of natural gases, advanced the theory of formation of low-mineralized waters in connection with the development of gas condensate deposits of Azerbaidzhan. He suggested that condensational ground waters are formed as a direct result of migration and accumulation of hydrocarbons; of all groups of natural waters, they can rightly be described

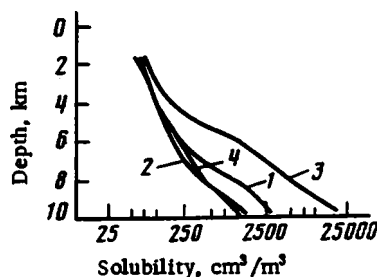


Fig. 1.

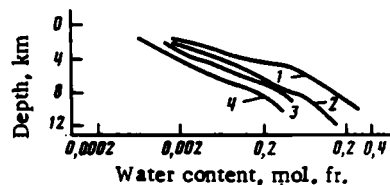


Fig. 2

Fig. 1. Methane moisture content versus depth in thermobaric conditions of oil and gas pressure basins in the southern USSR [8]. Basins: 1) Plainland Crimea; 2) South Caspian; 3) Dnieper-Donets; 4) Ciscarpathian.

Fig. 2. Solubility of water in oil in the thermobaric conditions of oil and gas water pressure in basins of the southern USSR. Basins: 1) South Caspian; 2) Ciscarpathian; 3) Crimean-Ciscaucasus; 4) Dnieper-Donets.

as oil water. The main cause of formation of condensational waters is the high solubility of water in several gaseous and liquid hydrocarbons. Figures 1 and 2 plot water solubility and methane water content versus occurrence depth of oil and gas deposits [8]. The curves illustrate that in principle it is possible to isolate condensation water from a homogeneous hydrocarbon fluid as it rises from deeper zones of the earth's crust to upper levels.

Kolodii [8] estimated that if oil rises from a depth of 8 km to a depth of 3 km, each cubic meter of a hydrocarbon mix will release 0.001-0.01 m³ of solution water (water dissolved in oil). As a result, a deposit containing 50×10^6 m³ of oil will release 5×10^4 m³ of water. For a water-oil contact area of 1 km², collector porosity of 15%, and residual water saturation of 20%, the water fringe under the deposit will be 0.4-4.0 m thick.

In the same conditions the transport of water by gaseous hydrocarbons will release from each cubic meter of gas (under normal conditions) 28-53 g of condensation water, which for a deposit of 5×10^9 m³ of gas will amount to $14 \times 10^5 - 2.6 \times 10^5$ m³ of water [8]. For the above water-oil contact porosity and residual saturation the water fringe will be 11-22 m thick. In a platformal environment with low slope angles of beds and a substantial area of gas-water contact, the fringe of desalted condensation waters can be very thin. For folded areas with steep beds and a small area of water-oil-gas contacts, the condensation (or solution) water beds can be tens of meters thick or more.

The determining factor in the formation of desalted condensation waters is the simultaneous condensation from a homogeneous gas-condensate system of heavy hydrocarbons into the liquid phase and the saturation of this phase with gas containing water vapors. The excess of these vapors is isolated into a separate phase, forming a dispersional system: gas-condensate-water [19]. The excess influx of the vapor phase (and therefore the possible formation of condensation waters in the structures of the South Caspian depression) is possible at depths of at least 3-4 km.

Generally, the origins of the desalted water fringe is only a part of the problem: after they are formed and isolated within the oil and gas trap, condensation waters begin to interact with the background waters of normal salinity; as a result, mineral content and composition of water may become homogenized. The practice of geological exploration and hydrogeological sampling, however, shows that desalted fringes uncovered by bore holes can often serve as an indicator of nearby oil and gas deposits and have helped in locating them [16].

We thus see various experimentally confirmed and theoretically analyzed phenomena that have been observed in nature and are associated with the development of desalted condensation waters. In this connection, another regularity is remarkable; it has been established in two of the largest gas deposits of western Siberia (Urengoi and Yamburg [1]).

A much lower salinity of bound water extracted from clay fractions of rocks within the deposit contours has been discovered there as compared with samples taken outside the contour. This may also confirm the desalting effect of condensation waters formed in connection with the gas deposits.

TABLE 1. Composition of Condensational Waters from Gas and Oil Deposits, Condensates of Gas-Vapor Jets from Hot Springs and Rainwater

Deposit, source (sample interval, m)	pH	Contents, mg/liter								Total salt content, mg/liter	Reference	
		Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	SiO ₂			
North Crimean trough												
Zadornen, well 11 (554—580)	7,0	29,9	—	35,3	7,1	21,3	19,8	152,6	7,3	266,0	[8]	
Cisrpathian												
Dashav, well 46 (610—625)	—	722,0	—	2,0	2,5	1065,0	9,1	91,5	5,4	1892,0	[8]	
Dnieper-Donets depression												
Pereshchepin, well 112	—	28,0	—	6,4	2,2	57,0	5,0	Not det'd.	3,2	106,0	[8]	
Rbal'sk, well 154 (1535—1590)	7,0	214,0	7,0	186,4	40,0	395,0	260,0	342,0	18,8	1477,0	[8]	
Central Asia												
Gazli, horizon IX, well 56	6,6	61,4	4,0	10,0	2,7	35,3	9,0	134,5	—	264,4	[11]	
Same, horizon X, well 153	6,0	10,6	Not det'd.	7,0	Not det'd.	5,6	2,2	38,8	—	68,4	[11]	
Western Siberia												
Medvezh'e, well 519*	7,95	124,0	3,1	15,2	1,5	149,6	—	163,5	5,2	462,1	—	
Same, well 1003*	7,42	38,6	3,1	43,2	4,9	138,3	—	36,6	2,6	267,3	—	
Urengoi, well 12212*	6,69	18,6	8,75	2,4	2,4	29,2	—	29,3	1,2	91,8	—	
Rioni Lowland (rainwater)												
Maltakva	6,05	0,92	0,25	1,15	0,23	1,34	2,06	3,78	0,5	10,6	[5]	
Kamchatka (gas-steam jets)												
Geysers	5,5	168,8	0,6	14,0	1,2	352,8	41,2	141,5	1,2	840,0	[9]	
Uzon, central fumarole field	6,85	15,4	0,2	Not det'd.	Not det'd.	8,6	37,9	22,0	2,6	100,0	[9]	

*Water samples collected by V. G. Kozlov, All-Union Scientific Institute of Natural Gas Research; analysis performed by N. I. Avtandilova, Geological Institute, USSR Academy of Sciences.

The chemical composition of condensation water is peculiar. It can be distorted by residual background waters. Of most interest for the chemical characterization of condensation waters are data obtained in the operation of gas deposits when formation settings are disrupted [11]. The fact that gas flows from the depths for a long time leaves no doubt that what is taken for analysis is condensation water rather than any other type of water (such as residual stratal water or technogenic water introduced during the drilling of exploration or development wells). The chemical characteristics of condensation waters are given in Table 1.

Condensation waters typically have an extremely low salt content. The salinity of these waters is sometimes similar to that of rainwater. Hydrocarbonates are the principal anions, but sometimes Cl^- concentration is higher than that of HCO_3^- . A heightened sulfate concentration is observed sometimes. Sodium is usually the main cation. The composition of trace elements has been studied little. Relatively heightened silica concentrations are assumed. The available data and the theoretical models of the migration of silica in the gas phase, however, suggest that its contents in condensation waters should be low. For comparison, Table 1 gives the composition of rainwater and steam-condensates of the highest-silica nitrogen-carbon dioxide hot springs, such as geysers. The table shows that mean silica concentrations in vapors are not high. Experimental data indicate that silica in vapors is proportional to vapor density [14], but also depends on the silica concentration in the initial water being evaporated. Condensation waters probably are similar. Generally, silica content in them depends on temperature, pressure (the formation depth of the oil and gas deposit), and silica content in the initial water from which the deep homogeneous fluid originated. This principle probably holds for other components as well.

The physicochemical characterizations of condensation waters usually stress the exceptionally low pH (normally, 5.5-6.5). This is probably due to the presence of CO_2 , invariably associated with hydrocarbon gases and likely to dissolve in water rapidly.

By their hydrochemistry, condensation waters of oil and gas deposits are thus similar to highly reactive water types, capable of active interaction with surrounding rocks.

The author has no data on oil and gas deposits with large amounts of condensation water determined reliably or on any detailed mineralogic and geochemical studies of rocks surrounding the hydrocarbon deposit. The analysis in this paper is based on a model of generalized geological settings which largely relies on the results of [8, 13]. For a quantitative evaluation of the geochemical role of condensation water we used a calculation model describing the development of a gas (or gas-condensate) deposit formed at a depth of 3 km with the original fluid rising from a depth 8 km. As gas deposit with a reserve of $5 \times 10^9 \text{ m}^3$ should then yield $2.6 \times 10^5 \text{ m}^3$ of condensation water [8]. It can be assumed [13] that the open porosity of arkosic sandstones in that case is 15% and that of cement 7%. Cement is represented by montmorillonite (we have also considered the cases of cement consisting of chlorite, hydromica, and a hydromica-montmorillonite mixed-layer mineral).

The methods of chemical thermodynamics, elaborated in [2, 28, 31, 32, and other publications], are used to appraise the direction and limits of alteration of the principal rock-forming minerals of the rocks that accumulate condensation waters.

The estimation of the free energies of the formation of minerals of variable composition (such as montmorillonite, hydromica, chlorite, and especially mixed-layer minerals) presents a certain difficulty in such calculations. We can be satisfied, however, by an approximate estimate of the thermodynamic parameters of these minerals. The matter is further simplified by the fact that the ionic force of these solutions is extremely low (usually under 0.03), so that the Debye-Hückel equation can be used in a second approximation to calculate the activity coefficients of the mobile reaction components: Na^{2+} , K^+ , Ca^{2+} , Mg^{2+} , and H^+ . The activity coefficients of H_2 and H_4SiO_4 are set equal to 1.

As an example of a graphic description of an equilibrium system, we present a diagram characterizing the equilibrium condition of the minerals albite-Na-montmorillonite-kaolinite-gibbsite (Fig. 3).

The distribution of the points describing the chemical composition of condensation waters (based on data of Table 1) is enclosed in the region corresponding to the equilibrium state of water solutions with gibbsite and kaolinite. This is also true for other equilibrium systems, such as chlorite-Mg-montmorillonite-kaolinite-gibbsite; Ca-plagioclase-Ca-

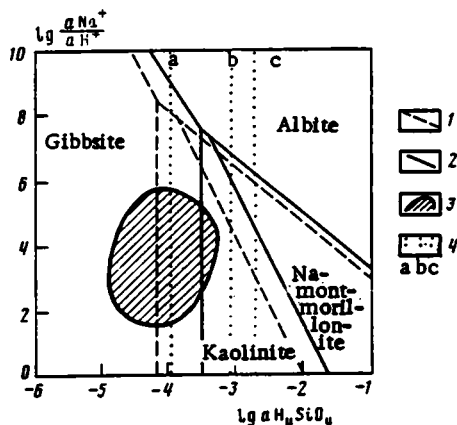


Fig. 3.

Fig. 3. Diagrams of equilibrium states of the system $\text{HCl-H}_2\text{O-Al}_2\text{O}_3\text{-Na}_2\text{O-SiO}_2$ at various temperatures: 1) at 25°C (after [28]); 2) at 100°C (author's data); 3) occurrence field of condensation water; 4) saturation level of quartz (a - at 25°C, b - at 100°C) and amorphous silica (c - at 25°C).

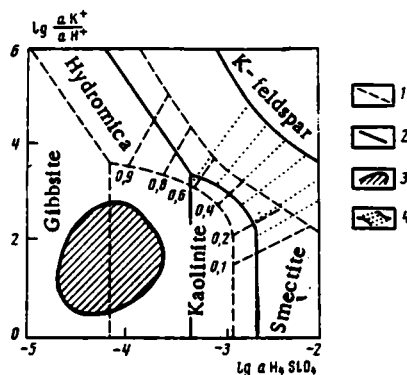


Fig. 4

Fig. 4. Diagrams of the equilibrium state of the system $\text{HCl-Al}_2\text{O}_3\text{-K}_2\text{O-SiO}_2$ at various temperatures: 1) at 25°C (after [30]); 2) at 100°C (author's data); 3) occurrence field of condensation waters; 4) levels of a hydromicaceous component in the occurrence field of hydromica-smectite mixed-layer mineral.

montmorillonite-kaolinite-gibbsite; and potash feldspar-muscovite-K-montmorillonite-kaolinite-gibbsite; or systems that include the existence of mixed-layer minerals (Fig. 4).

The diagrams indicate that the composition of condensation waters based on thermodynamic estimates allows viewing these waters as an active factor in the alteration of rock-forming minerals. In the early stages the process was directed at complete hydrolytic decomposition of the minerals. As lixiviation products accumulate in the solution, the process stabilizes at the equilibrium level of a solution with kaolinite; when kaolinite attains an equilibrium with minerals of a higher silicification degree (smectite, hydromica, chlorite, or mixed-layer minerals) the process should stop. This is confirmed by in situ observations in deposits.

Kaolinization reaction of clay minerals and their thermodynamic parameters are described by equations of the reactions that are necessary for estimating the reaction constants. These equations are given in Tables 2 and 3.

With these data it was possible to compute the constants of kaolinization reactions for normal conditions with the equation

$$\Delta G_{\text{react}}^0 = -1.364 \lg K_{298.15}, \quad (1)$$

where $\Delta G_{\text{react}}^0$ is the standard free energy of reaction; and K is the reaction constant.

For calculating the constants of reactions occurring at higher temperatures, several calculation methods are used (see Table 3). The simplest but least accurate method is based on the van t'Hoff equation:

$$\frac{dK}{dT} = \frac{\Delta H_{\text{react}}^0}{T^2}. \quad (2)$$

When this equation is used in a relatively small temperature interval, and ΔH_{react} is assumed to be a constant, acceptable estimates can be calculated conveniently. Integrating (2) and converting natural to decimal logarithms, we obtain

$$2.303 \lg \frac{K_{T_2}}{K_{T_1}} = -\frac{\Delta H_{\text{react}}^0}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right), \quad (3)$$

TABLE 2. Thermodynamic Parameters of Clay Minerals and the Principal Components of Water Used in Equilibrium Evaluations

Clay mineral and solution components	$\Delta H_{298,15}^0$, ccal/mol	$\Delta G_{298,15}^0$, ccal/mol	Reference
Na-montmorillonite			
(Na _{0,33} Al _{2,33} Si _{9,67} O ₁₀ (OH) ₂	-1366,84	-1277,76	[29]
Chlorite Mg ₅ Al ₂ Si ₅ O ₁₀ (OH) ₂	-2109,84	-1954,8	[29]
Hydromica			
K _{0,6} Mg _{0,23} Al _{1,3} Si _{3,5} O ₁₀ (OH) ₂	-1390,8	1300,98	[29]
Kaolinite			
Al ₂ Si ₂ O ₅ (OH) ₄	-979,6	-903,0	[15]
H ₄ SiO ₄	-349,46	-312,64	[15]
H ₂ O	-68,315	-56,688	[15]
Na ⁺	-57,469	-62,672	[15]
K ⁺	-60,04	-67,466	[2]
Mg ²⁺	-110,36	-108,81	[15]
H ⁺	0	0	[2]

where KT_1 is the reaction constant at 25°C; KT_2 is the reaction constant to be estimated for a given temperature; $\Delta H_{0\text{react}}$ is the enthalpy reaction; and R is the universal gas constant.

Equation (3) was used to calculate the constants of reactions II and III (see Table 3) evolving at 100°C. Normal and relatively high-temperature conditions were thus studied. The highest temperature range was chosen because the characteristics of condensation waters can be observed in it.

Since the natural systems are closed, the principle of thermodynamic equilibrium in the development of processes is justified. This makes it possible to estimate the development of the kaolinization process as resulting from condensation water activity. The maximum possible values of the mobile components of reactions must be estimated for this purpose.

As an illustration, we will consider kaolinization of Na-smectite (reaction I) (see Table 3).

The mobile components of this reaction can be described by the following formulas:

$$\log \frac{a \text{Na}^+}{a \text{H}^+} = \frac{\lg K - 2,68 \lg a \text{H}_4\text{SiO}_4}{0,66}; \quad (4)$$

$$\log a \text{H}_4\text{SiO}_4 = \frac{\lg K - 0,66 \lg \frac{a \text{Na}^+}{a \text{H}^+}}{2,68}. \quad (5)$$

The influx of Na²⁺ ions to solution is caused by the action of protons upon the crystalline lattice of the mineral. The efflux of sodium will be associated with a relative rise in pH of the water medium. As Na- (or K-) montmorillonite interacts with condensation waters, the value of $\log a \text{Na}^+ / \log a \text{H}^+$ (respectively, $\log a \text{K}^+ / \log a \text{H}^+$) will be changed slightly or rise a little. The value of $\log a \text{Na}^+ / \log a \text{H}^+$ for condensation waters varies from 1.41 to 5.46 (an average of 3.435). Considering the value of relation (5), we can determine the concentration of silica for an equilibrium state of the kaolinite-Na-montmorillonite system computed at 100°C. The maximum silica concentration in H₄SiO₄ is 245 mg/liter.

In a similar fashion we calculate the chemical components in the solution, which determine the coexistence of chlorite-kaolinite and hydromica-kaolinite minerals. The silica concentration that can support the equilibrium coexistence of chlorite-kaolinite is 80 mg/liter; for kaolinite-hydromica it is 76 mg/liter (at 100°C). With the diagram of Fig. 4 we can estimate approximately the maximum silica concentration at 100°C at which kaolinite can coexist with a mixed-layer mineral such as hydromica-smectite; in this case it is 170 mg/liter.

The estimates of kaolinization degree are based on the data of [8, 13]; we assume that in terrigenous strata, where a gas or gas-condensate deposit was formed, the rock cement consisting in this case of Na-montmorillonite amounts to 7%, the open porosity 15%, and the volumetric weight of montmorillonite 1.8 g/cm³. After trivial calculations, we determine

TABLE 3. Thermodynamic Parameters and Constants of Kaolinization Reactions of Clay Minerals

Kaolinization reactions of Na-smectite (I), chlorite (II), and hydromica (III)	Reaction constant	$\Delta H_{298,15}^{\circ}$ ccal/mol	$\Delta G_{298,15}^{\circ}$ ccal/mol	$\lg K_{298,15}$	$\lg K_{373,15}$
I $2Na_{0,33}Al_{2,33}Si_{3,67}O_{10}OH_2 + 0,66H^+ + 7,69H_2O = 2,33Al_2Si_2O_5(OH)_4 + 0,66Na^+ + 2,68H_4SiO_4$	$K = \frac{[Na^+]^{0,66}[H_4SiO_4]^{2,68}}{[H^+]^{0,66}}$	4,968	7,084	-5,19	-4,64
II $Mg_3Al_2Si_2O_{10}(OH)_2 + 10H^+ = Al_2Si_2O_5(OH)_4 + 5H_2O + 5Mg^{2+} + H_4SiO_4$	$K = \frac{[Mg^{2+}]^5[H_4SiO_4]}{[H^+]^{10}}$	-112,60	-88,33	64,75	48,15
III $2K_{0,8}Mg_{0,22}Al_{2,3}Si_{3,5} \times O_{10}(OH)_2 + 2,2H^+ + 6,3H_2O = 2,3Al_2Si_2O_5(OH)_4 + 2,4H_4SiO_4 + 1,2K^+ + 0,5Mg^{2+}$	$K = \frac{[K^+]^{1,2}[Mg^{2+}]^{0,5}[H_4SiO_4]^{2,4}}{[H^+]^{2,2}}$	-7,34	-3,61	2,65	1,57

Note. For reaction I, $K_{373,15}$ was computed was the heat capacity equation from [15]; for reactions II and II, with the van t'Hoff equation.

that when condensation waters interact with rock cement, 0.1-0.15% of the volume of cement in the activity sphere of this type of water should be kaolinized.

Other interactions are disregarded, e.g., the possibility of silica fixation by organic compounds such as resins, naphthenes, etc., or scattering of condensation waters and their interaction with ordinary formation waters.

A gas (or gas-condensate) deposit with condensation waters collected at its bottom is interpreted as a static externally invariable closed system; the reaction products in the system have no free outlet and accumulate in the deposit's fringe. So-called solution waters display more diverse compositions than do condensation waters but are developed on a much smaller scale.

Process of kaolinization of other mineralogic cement types (chlorite, hydromica, or mixed-layer minerals) have similar characteristics.

Despite the pronounced thermodynamic imbalances of condensation waters relative to rock-forming minerals, their geochemical activity is limited.

The presence of condensation and solution waters is more noticeable the more contrastive are pressures at the levels where oil and gas fluids originate and accumulate in a trap. Waters of these types should be absent in oil and gas deposits formed in situ and containing hydrocarbons that have never been subjected to any substantial migration.

Oil and gas traps in other situations can function as intermediate chambers into which a hydrocarbon fluid migrates periodically (so-called collapse of deposits). This may create conditions for periodic renewal of accumulations of condensational and solutational waters. Kaolinization plays a definitive role and, as mentioned earlier, can be observed in mineral associations inside the contours of oil and gas deposits. The contact with liquid hydrocarbons can activate quartz regeneration when silica accumulates in the solution and thus prolong the kaolinization process. The importance of kaolinization due to the activity of this type of waters even in a most favorable case is unlikely to exceed a few percentage points of the total amount of clay cement in the surrounding rocks. Authigenic kaolinite, however, sometimes amounts to 50 or more percent of the total clay matter in such situations [13]. The scale of hydrochemical inversions in oil and gas provinces is remarkably larger than what can be attributed to desalting of ground water caused by condensation water (northern Sakhalin, western Siberia). Low-salt waters in oil and gas provinces at great depths could be a product of dehydration of clays and aquagenic organic materials, efflux of bound water, and hydromicatization of montmorillonites. These geochemical phenomena could affect the development history of a sedimentary basin and intensify the effect of condensational or solutational waters.

Carbon dioxide lixiviation apparently plays the most important part in catagenetic (or hydrogenic) kaolinization.

In oil and gas provinces the oxidation of organic materials usually adds some CO₂ to gases of the methane series. Carbon dioxide lixiviation, however, is usually noticeable where coaly anhydride is of a metamorphogenic origin. The CO₂ concentrations in such cases can be higher than methane concentrations, and partial gas pressures can reach several atmospheres or even tens of atmospheres. These carbon dioxide fluids constitute an independent province in the modern orogenic belt, not associated with oil and gas formation processes. However, they also occur in oil and gas regions (western Siberia and northern Sakhalin) [3, 21] and tend to be associated with tectonically active zones: faults and rifts. Prolonged aggressive activity of these waters apparently promotes the development of afa-cial vertical zones with metasomatic kaolinite forming so-called kaolinitic columns [25]. The structures they form have optimal collector properties and sometimes become containers of oil and gas deposits.

* * *

The following conclusions can be drawn from these observations.

1. Both the concept of "retardation" and the concept of activization of catagenesis during the formation of oil and gas and gas-condensate deposits reflect the different roles of the hydrogeochemical media participating in this complex and conflict-affected process.
2. The more contrastive the P-T conditions at the level where the homogeneous hydrocarbon fluid originates and generates a deposit, the more likely and noticeable will be alteration of rocks by condensation and solutinal waters.
3. By their thermodynamic parameters condensation waters act as a potentially active factor in catagenetic rock alteration. Since the scale of their activity is limited and the system is closed, their contribution to this process is reduced.
4. Studies with the methods of chemical thermodynamics have shown that the kaolinization of smectites, hydromicas, chlorites, and other clay minerals of rock cement caused by condensation water can affect up to 0.1-0.15% (of the total amount of cement), and as high as a few percentage points in the most favorable settings.
5. The large scale of kaolinization (50% and more of the total mineral composition of cement) is due to the activity of deep carbon dioxide fluids formed as a result of metamorphic processes.

LITERATURE CITED

1. V. Kh. Akhiyarov and F. Z. Khafizov, "Paleohydrogeologic method of study of the formation conditions of oil and gas deposits," *Sov. Geol.*, No. 3, 53-56 (1985).
2. R. M. Garrels and C. L. Crist, *Solutions, Minerals, Equilibrium* [Russian translation], Mir, Moscow (1968).
3. *Hydrogeology of the USSR* [in Russian], Nedra, Moscow (1972).
4. A. I. Gritsenko, "The influence of water on phase transitions of gas-condensate mixes," *Gazovoe Delo*, No. 4, 3-11 (1964).
5. V. P. Zverev, *Ground Water and Its Role in Migration of Chemical Elements* [in Russian], Nedra, Moscow (1982).
6. T. T. Klubova, *Clay Minerals and Their Role in the Genesis, Migration, and Accumulation of Oil* [in Russian], Dissertation for the degree of Doctor of Geological-Mineralogical Sciences, IGIRGI, Moscow (1970).
7. V. V. Kolodii, *Underground Condensation and Solution Waters of Oil, Gas-Condensate, and Gas Deposits* [in Russian], Naukova, Dumka, Kiev (1975).
8. V. V. Kolodii, *Underground Waters of Oil and Gas Provinces and Their Role in Oil Migration and Accumulation* [in Russian], Naukova, Dumka, Kiev (1983).
9. V. I. Kononov, *Influence of Natural and Artificial Heat Sources on the Chemical Composition of Groundwaters* [in Russian], Nauka, Moscow (1965).
10. A. É. Kontorovich and A. A. Trofimuk, "A methodology for study of the history of oil and gas deposits," *Geol. Nefti Gaza*, No. 7, 18-24 (1973).
11. V. N. Kontsenshtein, *Violation of Formation Water Equilibrium in the Development of Oil and Gas Deposits* [in Russian], Nedra, Moscow (1980).

12. V. M. Lazareva and E. N. Elizarova, "Regularities of the composition of clay minerals and bitumens in productive horizons and caps of Lower Cretaceous sediments of the western Ciscaucasus," *Neftegaz. Geol. Geofiz.*, No. 8, 31-37 (1969).
13. B. A. Lebedev, G. B. Aristova, E. G. Bro, et al., "The influence of epigenetic processes on the parameters of collectors and caps in Mesozoic sediments of the Western Siberian depression," *Tr. VNIGRI*, No. 361 (1976).
14. B. M. Mitsyuk and L. I. Gorogotskaya, *Physical and Chemical Alterations of Silica During Metamorphism* [in Russian], Naukova Dumka, Kiev (1980).
15. G. B. Naumov, B. N. Ryzhenko, and I. L. Khodakovskii, *A Handbook of Thermodynamic Constants* [in Russian], Atomizdat, Moscow (1971).
16. A. M. Nikanorov, *Methods of Hydrogeological Oil and Gas Exploration* [in Russian], Nedra, Moscow (1977).
17. G. N. Perozio, "Catagenesis and deep epigenesis in granular oil collectors at the Ust'-Balyk deposit" [Russian translation], in: *Postsedimentary Alterations of Sedimentary Rocks in Siberia* [in Russian], Nauka, Moscow (1967), pp. 70-98.
18. V. I. Petrenko, "Dynamics and phase transitions of ground waters during the development of gas-condensate deposits," *Izv. Akad. Nauk SSSR, Ser. Geol.*, No. 1, 116-129, (1982).
19. V. I. Petrenko and S. S. Zavodnoi, "The role of phase transitions in hydrocarbon-water systems in the formation of low-salt water fringes," *Dokl. Akad. Nauk SSSR*, 278, No. 5, 1196-1199 (1984).
20. G. É. Prozorovich, O. G. Zaripov, and Z. L. Valyuzhenich, *Lithology of Oil and Gas Deposits and the Central Parts of the West Siberian Depression* [in Russian], ZapSibNiGRI, Tyumen (1970).
21. A. A. Rozin and Z. Ya. Serdyuk, "Alteration of the composition of ground water and rocks in the West Siberian plate due to the effects of carbon dioxide in the earth's interior," *Litol. Polezn. Iskop.*, No. 4, 102-114 (1970).
22. R. S. Sakhibgareev, *Mineralogy of Clays of Productive Strata of the Deposits in Surtuk Oil Region* [in Russian], Dissertation for the degree of Candidate of Geological-Mineralogical Sciences, IGIRGI, Moscow (1968).
23. *Modern Problems of Geology and Geochemistry of Fossil Fuels* [in Russian], Moscow State Univ. (1986).
24. B. I. Sultanov, "Deep condensation waters of gas-condensate deposits and their formation conditions," *Dokl. Akad. Nauk AzSSR*, 17, No. 12, 1165-1167 (1961).
25. P. P. Timofeev, A. G. Kossovskaya, V. D. Shutov, et al., "New concepts in the theory of the stages of sedimentary rock formation," *Litol. Polezn. Iskop.*, No. 3, 58-83 (1974).
26. I. N. Ushatinskii, "Mineralogy and geochemistry of the clay matter of oil and gas deposits in western Siberia," Dissertation, Doctor of Geological-Mineralogical Sciences, Institut Geol. i Geofiz., Academy of Sciences of the USSR, Novosibirsk (1973).
27. R. M. Yurkova, "Studies of postsedimentary alterations of sandstones of oil and gas beds in northern Sakhalin," *Litol. Polezn. Iskop.*, No. 3, 20-32 (1969).
28. H. C. Helgeson, T. H. Brown, and K. H. Leeper, *Handbook of Theoretical Activity Diagrams Depicting Chemical Equilibria in Geological Systems Involving Solid and Aqueous Phase at 1 atm. and 0° and 300°C*, San Francisco (1969).
29. H. C. Helgeson, I. M. Delaney, H. W. Nesbitt, and D. K. Bird, "Summary and critique of the thermodynamic properties of rock-forming minerals," *Am. J. Sci.*, 278-A, 229 (1978).
30. H. W. Nesbitt, "A chemical equilibrium model for the Illinois Basin formation waters," *Am. J. Sci.*, 285, No. 5, 436-455 (1985).
31. T. Paces, "Chemical characteristics and equilibration in natural water-felsic rock-CO₂ system," *Geochim. Cosmochim. Acta*, 36, 217-240 (1972).
32. I. Tardy, "Characterization of the principal weathering types by the geochemistry of waters from zoned European and African crystalline massifs," *Chem. Geol.*, 7, No. 2, 253-271 (1971).

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